



**University of Warsaw**  
**Faculty of Chemistry**



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Summary of scientific and teaching accomplishments  
setting the basis for the habilitation procedure

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## 1. First and Last Names

Wojciech Aleksander Hyk

## 2. Diplomas and scientific degrees

- 2011 – certificate of TrainMiC Trainer (Training in Metrology in Chemistry: Principles and Applications of Metrology in Chemistry), Joint Research Center, European Commission, Geel, Belgium
- 2000 – Ph. D. in chemistry, Faculty of Chemistry, University of Warsaw, title of the Ph. D. thesis: „Diffusional and Migrational Transport of Molecules and Ions to Microelectrodes in Various Media”, supervisor: prof. dr hab. Zbigniew Stojek
- 1995 – M. Sc. in chemistry, Faculty of Chemistry, University of Warsaw

## 3. History of employment in scientific institutions

- since 2002: assistant professor and web administrator, Faculty of Chemistry, University of Warsaw
- 2000 – 2002: assistant, Faculty of Chemistry, University of Warsaw

## 4. Indication of achievements according to Art. 16 Paragraph 2 of the Act of Laws from 14 March 2003 on Academic Degrees (Journal of Laws no. 65, item 595 as amended)

### 4. A Title of scientific achievement

Publication cycle: „**Diffusion and Migration of Molecules and Ions in Micro- and Nano-Electrochemical Systems**”

### 4. B List of scientific publications setting the basis for habilitation proceedings

	Authors, title, editor or journal, volume, year, pages	IF	Number of citations
H1	<b>W. Hyk*</b> , A. Nowicka, Z. Stojek “Direct determination of diffusion coefficients of substrate and product by chronoamperometric techniques at microelectrodes for any level of ionic support” <i>Anal. Chem.</i> , 74 (2002) 149-157.	5.856	23

W. Hyk (70%): author of the theoretical fundamentals and the procedure for the practical realization of the method for the determination of both: substrate and product of an electrode process using chronoamperometric measurements under the conditions of supporting electrolyte deficit; preparation of the experimental work; participation in chronoamperometric and voltammetric measurements; interpretation of the data obtained; concept of the manuscript layout and its preparation (text, tables, figures); corresponding author.

H2	<b>W. Hyk*</b> , Z. Stojek “Generalized theory of steady-state voltammetry without supporting electrolyte. Effect of product- and substrate diffusion coefficient diversity” <i>Anal. Chem.</i> , 74 (2002) 4805-4813.	5.856	14
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W. Hyk (85%): theory of the mixed diffusional and migrational transport to microelectrodes in the absence of supporting electrolyte: formulation of the problem, concept of the method for the integration of the transport equations, analysis and interpretation of the integrals (solutions) obtained; concept of the new method for the determination of the product of the electrode process using steady-state voltammetry in supporting-electrolyte free system; experimental work - voltammetric measurements and data interpretation; concept of the manuscript layout and its preparation (text, tables, figures); corresponding author.

H3	A. Nowicka, <b>W. Hyk</b> , Z. Stojek, M. Ciszowska „Parallel electrode processes in absence of supporting electrolyte. Further strong enhancement or depression of transport of ionic species” <i>Pol. J. Chem.</i> , 78 (2004) 1553-1566.	0.393	1
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W. Hyk (50%): theoretical and experimental concept of parallel electrode processes in the absence of supporting electrolyte; participation in interpretation of the experimental data obtained; participation in the manuscript preparation.

H4	<b>W. Hyk*</b> , A. Nowicka, B. Misterkiewicz, Z. Stojek „The extreme migrational enhancement of faradaic current at microelectrodes: experimental studies on sodium ( $\pm$ )-(6,8-diferrocenylmethylthio)octanoate electrooxidation” <i>J. Electroanal. Chem.</i> , 575 (2005) 321-328.	2.905	2
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W. Hyk (60%): design of the redox system consisting of two appropriately linked ferrocene groups that undergoes the charge reversal electrode process; participation in the establishment of the conditions for the custom synthesis of the compound; participation in the voltammetric measurements using microelectrodes and electrodes of regular size; participation in spectrophotometric measurements; theoretical modeling of the strong enhancement of the faradaic current for such the redox system in the absence of supporting electrolyte excess; interpretation of the experimental data obtained; concept of the manuscript layout and its preparation (text, tables, figures); corresponding author.

H5	<b>W. Hyk*</b> , Z. Stojek “General theory for migrational voltammetry. Strong influence of diversity in redox species diffusivities on charge reversal electrode processes” <i>Anal. Chem.</i> , 77 (2005) 6481-6486.	5.856	14
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W. Hyk (85%): general theory of the mixed diffusional and migrational transport to microelectrodes under the conditions of varying content of supporting electrolyte: formulation of the problem, concept of the method for the integration of the transport equations, analysis and interpretation of the integrals (solutions) obtained with the special emphasis to charge reversal electrode processes; validation of the theoretical predictions for this class of electrode processes using the experimental data obtained in the previous work; data interpretation; concept of the manuscript layout and its preparation (text, tables, figures); corresponding author.

H6	<b>W. Hyk*</b> , J. Augustynski “Steady-state operation of porous photoelectrochemical cells under the conditions of mixed diffusional and migrational mass transport – Theory” <i>J. Electrochem. Soc.</i> , 153 (2006) A2326-A2341.	2.590	6
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W. Hyk (90%): theory of the mixed diffusional and migrational transport in dye-sensitized solar cells: formulation of the problem, concept of the method for the integration of the transport equations, analysis and interpretation of the integrals (solutions) obtained; optimization of the construction of the photoelectrochemical cells according to the theoretical predictions of the model; concept of the manuscript layout and its preparation (text, tables, figures); corresponding author.

H7	<b>W. Hyk*</b> , M. Karbarz, B. Misterkiewicz, Z. Stojek “Voltammetric Studies of Diffusional and Migrational Transport of Ferrocene Derivative of Tripeptide Glutathione” <i>J. Phys. Chem. B</i> , 111 (2007) 13090-13096.	3.696	6
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W. Hyk (65%): design of the redox system consisting of the ferrocene moiety linked with biologically active (tripeptide glutathione) molecule; participation in the voltammetric measurements using microelectrodes and electrodes of regular size; theoretical derivation of the microelectrode response due to the electrooxidation of the redox system neutralized with a strong base in two consecutive steps under the conditions of supporting electrolyte deficit; molecular-mechanics calculations of the molecule geometry; validation of the theoretical predictions using the voltammetric data obtained; interpretation of the obtained results; concept of the manuscript layout and its preparation (text, tables, figures); corresponding author.

H8	M. Karbarz, <b>W. Hyk*</b> , B. Misterkiewicz, Z. Stojek “pH affected migrational transport of ferrocene derivative of L-cysteine in aqueous solutions: Voltammetric studies” <i>Electrochim. Acta</i> , 54 (2009) 1263–1268.	3.832	3
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W. Hyk (50%): design of the redox system consisting of the ferrocene moiety linked with biologically active (L-cysteine) molecule; participation in the voltammetric measurements using microelectrodes; theoretical derivation of the microelectrode response due to the electrooxidation of the redox system under the conditions of varying content of supporting electrolyte and at different pH values; calculations of diffusion coefficient of the redox system; validation of the theoretical predictions using the voltammetric data obtained; interpretation of the obtained results; participation in the manuscript preparation (text, tables, figures); corresponding author.

H9	<b>W. Hyk</b> , Z. Stojek, “Microelectrodes for Electroanalytical Chemistry” in Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.), John Wiley & Sons Ltd., Chichester, S1-S3 (2010) 1115-1134.	-	-
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W. Hyk (50%): reviewing the theoretical models on diffusional and migrational transport to microelectrodes; participation in preparation of the manuscript (text, tables, all figures).

H10	<b>W. Hyk*</b> , Z. Stojek “Thin and Ultra-Thin Layer Dual Electrode Electrochemistry: Theory of Steady-State Voltammetry without Supporting Electrolyte” <i>Electrochemistry Communications</i> , (2013) DOI:10.1016/j.elecom.2013.06.010	4.859	-
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W. Hyk (90%): theory of the mixed diffusional and migrational transport in thin and ultra-thin layer dual electrode systems (including nanogap devices) in the absence of supporting electrolyte: formulation of the problem, concept of the method for the integration of the transport equations, analysis and interpretation of the integrals (solutions) obtained; concept of the manuscript layout and its preparation (text, tables, figures); corresponding author.

<b>Sum:</b>	<b>35.843</b>	<b>69</b>
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IF and number of citations are based on the Web of Science and Journal Citation Reports databases (June 03, 2013).

#### **4. C Summary of the scientific goals and major results of the presented publications (description of the scientific achievement)**

The series of publications presented as a basis for the habilitation, involves three major aspects of the electrochemical studies of electrode processes carried out under the conditions of varying content of supporting electrolyte. These include:

- theory of the mixed diffusional and migrational transport derived analytically for various boundary conditions defining various electrochemical systems under the steady-state conditions;
- new methods for the determination of both: substrate and product of electrode processes under the conditions of supporting electrolyte deficit;
- experimental verification of the theoretical predictions using the newly synthesized (in cooperation) redox systems that exhibit desired transport properties and obtained by attaching various molecules to the ferrocene moiety(ies).

#### **I. Introduction – electrochemistry with no supporting electrolyte**

The advantages of performing electrochemical measurements in supporting-electrolyte free systems are evident. First of all, they allow one to explore new research domains inaccessible for classical electrochemical approach (fully supported experiments) [H9]. These include:

- investigation of systems where deliberate introduction of supporting electrolyte is either impossible or inappropriate (solvents of low dielectric permittivity, solid state samples, environmental and biological samples);
- determination of transport and kinetic parameters unaffected by large electrolyte concentration and, therefore, comparable to the results obtained by non-electrochemical methods;
- examination of diffusional-migrational mass transport rate via specific enhancement or depression of recorded faradaic currents of electrode processes differentiated by charge numbers of the redox species.

Elimination of an excess supporting ions allows one to avoid their specific adsorption on the electrode surface, possible interactions with the electroactive species (including competitive chemical reaction between supporting ions and redox system), and introduction of uncontrolled amounts of chemical impurities to the system. On the other hand as the amount of supporting electrolyte decreases some inconvenient problems appear. The ohmic-potential drop (*IR*-drop) becomes significant factor that controls the electrode process overpotential. It narrows the potential window accessible to the electroactive species and distorts the shape of the electrode response. The *IR*-drop originates from the uncompensated electric field within the system. The latter induces an extra contribution (migrational transport) to the overall mass transport. Thus, in addition to diffusion, migration starts to control the mass transport of the redox species.

The exploration of the systems where transport is affected by migration required, therefore, both the experimental setup and theoretical modeling of the mass transport to be developed. The large working electrodes (conventionally-sized or macroelectrodes) and potentiostats of relatively small input impedance had to be replaced with microelectrodes and potentiostats of large input impedance, respectively. Microelectrodes - because of their small sizes - reduce substantially the magnitude of the measured current and, in consequence, lower the magnitude of *IR*-drop and its negative effect on the electrochemical signal.

In the theoretical modeling an extra contribution (migrational transport) to the overall mass transport had to be taken into account. An incorporation of a migration term into the transport equations introduced an extra terms and an extra variable - the electrostatic potential - to the transport equations (govern by the Fick's laws).

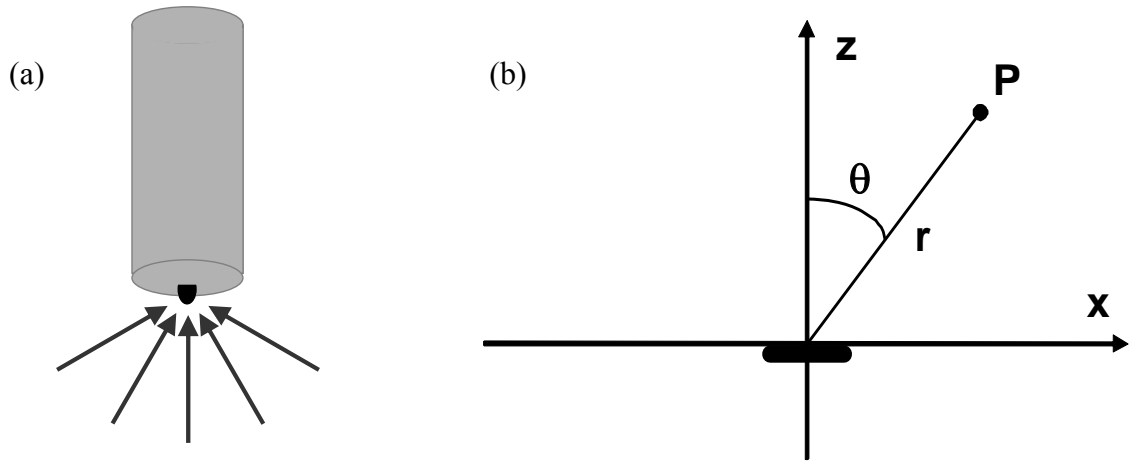
Nowadays microelectrodes are routinely employed for the electrochemical and electroanalytical studies of the transport-based problems coupled to heterogeneous electron transfer under the conditions of varying content of supporting electrolyte. The experimental and theoretical aspects of microelectrode electrochemistry (including electrochemical techniques, experimental conditions and detailed theoretical description of mass transport to microelectrodes under the diffusional –migrational conditions) are very well documented.

Compared to microelectrodes, nanoscale electrodes are expected to exhibit enhanced performance. As dimensions of the electrodes reach the nano regime in addition to the advantageous properties previously listed for microelectrodes, which are further magnified, new ones arise. These include: ultra fast and substantially amplified mass transport to the electrode, higher current densities giving rise to an increase in the ratio of faradaic to charging current, higher signal to noise ratios, steady-state conditions attained at very short time regimes, low depletion of electroactive species, drastically lowered limit of the amount of supporting electrolyte needed for the fully-supported measurements.

## **II. Theoretical modeling of diffusional and migrational transport**

### **II.1 Semi-infinite transport to microelectrodes with no supporting electrolyte [H2]**

The first research challenge in the theoretical modeling was focused on the derivation of the analytical solutions of the mixed diffusional and migrational semi-infinite transport to hemispherical microelectrodes and, consequently, on predictions of the magnitude of the limiting currents under the steady – state conditions in the absence of supporting electrolyte. The integration of the transport equations that do not impose any limitation on the magnitude of the species diffusivities was the pioneering task. The scheme of the model system treated by the theory and the coordinate system used are presented in Figure 1.



**Figure 1.** Schematic representation of hemispherical microelectrode and direction of mass transport to its surface (a), and definition of spherical (disk/hemispherical microelectrode) coordinates (a point P is located in any plane that is orthogonal to the insulating plane in which the electrode is embedded) (b).

In a system containing no added inert electrolyte, both diffusion and migration contribute to the total flux of the transported substance. The flux can be represented by the Nernst-Planck equation which, when applied to the transport field of spherical symmetry under the steady-state conditions, and written for each of the three solutes (i.e.  $S$ ,  $P$ , and  $X$  - the substrate, the product, and the counterion of the substrate (if it is charged), respectively) constitutes a system of three differential equations

$$\frac{dC_S}{dr} + \frac{z_S F}{RT} C_S \frac{d\Phi}{dr} = -\frac{I}{2\pi n F D_S r^2}$$

$$\frac{dC_P}{dr} + \frac{z_P F}{RT} C_P \frac{d\Phi}{dr} = \frac{I}{2\pi n F D_P r^2}$$

$$\frac{dC_X}{dr} + \frac{z_X F}{RT} C_X \frac{d\Phi}{dr} = 0$$

The set of the above equations contains four unknown functions, i.e.  $C_S$ ,  $C_P$ ,  $C_X$ , and  $\Phi$ . It can be made solvable by adding an extra relation, e.g. the electroneutrality principle

$$z_S C_S + z_P C_P + z_X C_X = 0$$

and the following boundary conditions

$$r \rightarrow \infty: \quad C_S \rightarrow C_S^b, \quad C_P \rightarrow 0, \quad C_X \rightarrow C_X^b = -\frac{z_S}{z_X} C_S^b, \quad \Phi \rightarrow \Phi^b.$$

where  $r$  is the radial distance from the electrode surface,  $D_i$ ,  $z_i$ , and  $C_i$  denote  $i$ -th species diffusion coefficient, charge number, and concentration, respectively,  $\Phi$  is the electrostatic potential in the solution,  $I$  is the faradaic current flowing through the surface of the working electrode, superscript  $b$  is related to the bulk of the solution where the substrate concentration  $C_S^b$  and the electrostatic potential  $\Phi^b$  are unchanged, and  $F$ ,  $R$ , and  $T$  have their usual meanings.

By applying the integration scheme based on the quasi-potential transformation, one was able to derive analytical solutions of the diffusional-migrational transport equations coupled to the boundary conditions stated above. The integration scheme was developed by me. The idea is to replace the distance variable with the electrostatic potential so that the integrals sought (the



concentrations of the species) are functions of the electrostatic potential. The transformed set of the transport equations takes the form:

$$\left( \frac{dc_s}{d\Psi} + z_s c_s \right) \frac{d\Psi}{dy} = -\frac{I}{I_d^L}$$

$$\left( \frac{dc_p}{d\Psi} + z_p c_p \right) \frac{d\Psi}{dy} = \frac{I}{\theta I_d^L}$$

$$\left( \frac{dc_x}{d\Psi} + z_x c_x \right) \frac{d\Psi}{dy} = 0$$

where  $c$  denotes the concentration (made dimensionless with respect to  $C_S^b$ ),  $y$  is the distance variable normalized with respect to the microelectrode radius,  $r_e$  ( $y = r_e / r$ ),  $\Psi$  denotes uncompensated electrostatic potential (made dimensionless with respect to the value of the electrostatic potential in the solution bulk  $\Phi^b$ , i.e.  $\Psi = F(\Phi - \Phi^b) / RT$ ),  $d\Psi / dy$  is the electrostatic potential gradient,  $I_d^L$  is the limiting current at hemispherical electrodes for the purely diffusional conditions ( $I_d^L = 2\pi nFD_S C_S^b r_e$ ),  $\theta$  is the ratio of the diffusion coefficients of the product and the substrate of the electrode process ( $\theta = D_P / D_S$ ).

The integration of the set of the differential transport equations leads to the analytical expressions. They describe the potential dependencies of the concentrations of the substrate, the product, and the counterion, respectively, and the variation of  $\Psi$  vs.  $I$  in an implicit form. They allow one to express quantitatively the key parameters characterizing the electrode processes of various classes at the microelectrodes, i.e. the magnitude of the limiting faradaic current, the electrostatic potential across the cell, and the resistance. The theoretical predictions revealed that the absence of excess supporting electrolyte induces a great diversity in the microelectrode response as a result of different response to the charge numbers and diffusivities of electroactive species. The obtained expression are generalized versions of those derived with simplifying assumptions.

The limiting current can be expressed in the following form:

$$\frac{I^L}{I_d^L} = 1 - \frac{z_s}{z_x} \left\{ 1 - \frac{z_p(z_s - z_x)}{z_x(z_s - z_p)} \ln \left[ \frac{z_p(z_s - z_x)}{z_s(z_p - z_x)} \right] \right\} \quad \text{for } \theta = 1, \text{ any } z_s, z_p, z_s \neq z_p$$

$$\frac{I^L}{I_d^L} \rightarrow 1 \quad \text{for } z_s = 0, \text{ any } \theta \text{ and } z_p, z_s \neq z_p$$

$$\frac{I^L}{I_d^L} = \frac{z_x - z_s}{z_x} \quad \text{for } z_p = 0, \text{ any } \theta \text{ and } z_s, z_p \neq z_s$$

$$\frac{I^L}{I_d^L} = \frac{\theta}{\theta - 1} \left[ \frac{z_x - z_s}{z_x} + \frac{z_s(z_p - z_x)}{z_x z_p} e^{-z_x \Psi^L} \right] \quad \text{for } z_s z_p (\theta - 1) \neq 0 \text{ and } \text{sgn}(z_s) = \text{sgn}(z_p)$$

where the limiting electrostatic potential,  $\Psi^L$  is given by

$$\Psi^L = \frac{z_p - z_s \theta}{z_s \theta (z_p - z_x) - z_p (z_s - z_x)} \ln \left[ \frac{z_s (z_p - z_x)}{z_p (z_s - z_x)} \theta \right]$$

In general, it is not possible to derive an analytical expression for the migrational voltammetric curve (with the exception for some special cases discussed later), however, it is possible to construct a theoretical steady-state voltammogram for any combination of  $\theta$ ,  $z_s$ ,  $z_p$ , and  $z_x$  using the iterative procedure that employs the derived solutions of the diffusional-migrational transport equations. The proposed calculation scheme can be performed for both:

the processes controlled by the transport rate (the Nernstian conditions) as well as those controlled by the kinetics of the charge transfer (the Butler – Volmer conditions).

It is worth noting that the analytical expressions of the voltammetric curve recorded in the absence of supporting electrolyte can be derived analytically only for two cases:  $z_P = 0$  (charge neutralization processes) and  $z_P = z_X$  (charge reversal processes). The results for the reversible reactions are as follows

$$E = E^{0'} + \frac{RT}{z_S F} \ln \left( \frac{I_d^L}{I} \theta \right) + \frac{RT}{z_S F} \frac{I^L}{I_d^L} \ln \left( \frac{I^L - I}{I^L} \right)$$

$$E_{1/2} = E^{0'} + \frac{RT}{z_S F} \ln \left( \frac{2I_d^L}{I^L} \theta \right) - \frac{RT}{z_S F} \frac{I^L}{I_d^L} \ln 2$$

for charge neutralization processes, where  $\frac{I^L}{I_d^L} = \frac{z_X - z_S}{z_X}$ , and

$$E = E^{0'} + \frac{RT}{nF} \ln \left[ \frac{z_S}{z_P} \left( 1 + \frac{z_P(\theta - 1)}{\theta(z_S - z_P)} \frac{I}{I_d^L} \right)^\gamma - \frac{z_S}{z_P} \right] + \frac{RT}{F} \frac{(z_P - z_S \theta)}{z_S z_P (\theta - 1)} \ln \left[ 1 + \frac{z_P(\theta - 1)}{\theta(z_S - z_P)} \frac{I}{I_d^L} \right]$$

for charge reversal processes, where  $\gamma = \frac{z_S - z_P}{z_S(\theta - 1)}$ .

The most intriguing effects are expected for the processes that undergo with the reversal of the sign of electroactive-species charge numbers. According to the theoretical findings, the faradaic current for this class of electrode processes increases limitlessly as supporting electrolyte is totally eliminated from the system. As a result, instead of typical wave-shaped voltammograms (with plateau), ramp-shaped ones are predicted. This behavior is a direct consequence of the preservation of the electroneutrality principle which is incorporated into the theoretical models, since the substrate of the electrode process serves as the counterion to the product of the electrode process. Consequently, at a sufficiently positive (or negative) potential, migration starts to dominate the transport of the substrate and the current intensity is controlled entirely by the cell potential and, thus, obeys Ohm's law. The self-enhancement effect can be altered significantly by the  $\theta$  value. For  $\theta > 1$  the transformation of the ramp-shaped voltammogram to the common wave-shaped curve is predicted. A totally different behavior can be noticed for the case of  $\theta < 1$ . In such the situation the current grows even faster than it can be predicted by Ohm's law.

The theoretical modeling provided also another significant finding: the expression for the limiting current can be linearized with respect to the  $\theta$  parameter and can be represented as

$$\frac{I^L}{I_d^L} = \frac{I_1^L}{I_d^L} + a \ln(\theta)$$

where  $I_1^L$  is the limiting current calculated for a supporting electrolyte-free solution with the assumption of equal diffusion coefficients of the substrate and the product, and  $a$  is a function of  $z_S$ ,  $z_P$ , and  $z_X$  generated by the Taylor expansion. The numeric values of  $I_1^L / I_d^L$  and  $a$  for a monovalent counterion and for various  $z_S$  and  $z_P$  combinations likely to be encountered in practice can be easily tabulated.

The convenient form of the linear expression of  $I^L$  vs.  $\ln(\theta)$  made feasible the voltammetric determination of the product diffusion coefficient, if the values of the limiting currents recorded in the system containing no and excess supporting electrolyte are known.

Finally, it is worth emphasizing that the assumption of the steady-state conditions at sufficiently large overpotential makes the theoretical conclusions derived for the limiting current at hemispherical electrodes applicable to microelectrodes of disk and other geometries.

## II.2 Semi-infinite transport to microelectrodes under the conditions of varying content of supporting electrolyte [H5]

Derivation of a theoretical model that involves the changes in both: diffusion coefficients and concentration of supporting electrolyte was the continuation of the previous work. The model derived is a broad extension of the theory developed for the systems with no supporting electrolyte. The theoretical scheme obtained can be applied to any electrode process carried out in the presence of any number of non-electroactive ions. In this case the transport equations for the steady-state conditions, written for each solute, constitute the system of differential equations, which, after applying the normalization rules and quasi-potential transformation, takes the following form:

$$\left( \frac{dc_s}{d\Psi} + z_s c_s \right) \frac{d\Psi}{dy} = -\frac{I}{I_d^L}$$

$$\left( \frac{dc_p}{d\Psi} + z_p c_p \right) \frac{d\Psi}{dy} = \frac{I}{\theta I_d^L}$$

$$\left( \frac{dc_j}{d\Psi} + z_j c_j \right) \frac{d\Psi}{dy} = 0 \quad j = 1, \dots, N$$

where  $N$  is the number of supporting ions plus the substrate counterion. By adding the relation for the electroneutrality principle

$$z_s c_s + z_p c_p + \sum_{j=1}^N z_j c_j = 0$$

and the following boundary conditions

$$y \rightarrow 0: \quad c_s \rightarrow 1, \quad c_p \rightarrow 0, \quad c_j \rightarrow c_j^b, \quad \Psi \rightarrow 0$$

the set of the above equations becomes solvable.

The integration of the transport equations followed the procedure described in the previous section. The obtained analytical expressions (the potential dependencies of the concentrations of the substrate, the product and  $N$  electroinactive ions, and the electrostatic potential dependence on the current and the distance from the electrode surface) are the generalized versions of those derived for the supporting-electrolyte free system. They allow one to obtain quantitative information on the key parameters characterizing the electrode processes of various classes, i.e. the magnitude of the limiting faradaic current at microelectrodes, the electrostatic potential across the cell, and the resistance. The theoretical predictions revealed a great diversity in the microelectrode response as a result of different response to the charge numbers, diffusivities of electroactive species, and both: the content and the type of the supporting electrolyte(s) introduced to the system.

The corresponding analytical expressions describing the limiting faradaic current and the electrostatic potential across the cell can only be derived for the processes that generate univalent product from the substrate of any charge accompanied by the univalent counterion, and are carried out in the presence of at least a trace of supporting electrolyte consisting of univalent ions. This case covers electrooxidations producing univalent cations from an

anionic substrate and electroreductions generating univalent anions from a cationic substrate, i.e., the charge reversal processes of  $S^z \rightarrow P^\pm + ne$  type ( $n + z = \text{sgn}(n)$  and  $|n| \geq 2, N = 2$ ). The following expressions for the limiting electrostatic potential at the interface (limiting ohmic potential drop across the cell) and the limiting current are derived:

$$\Psi^L = -\text{sgn}(z) \frac{1 + |z|\theta}{1 + 2|z|\theta - |z|} \ln \left[ \frac{1 + 2\theta(\xi + |z|) - |z|}{2\theta\xi} \right]$$

$$\frac{I^L}{I_d^L} = \frac{\theta}{\theta - 1} \left\{ 1 + |z| + 2\xi \left[ 1 - \exp(-\text{sgn}(z)\Psi^L) \right] \right\}$$

where  $\xi$  is the support ratio, defined as  $C_{se}^b / C_S^b$  (the ratio of the bulk concentrations of supporting electrolyte and the substrate).

In general, the derived analytical solutions of the transport equations provide tools for the construction of a steady-state voltammogram for any class of electrode processes, i.e. for any  $\theta, c_j^b, z_S, z_P,$  and  $z_j$  set. By constructing the steady-state voltammogram one is able to extract the limiting characteristics for any type of the electrode process. The algorithm consists of several steps to be performed iteratively. It requires the calculation of the surface concentrations of the substrate and the product using the actual value of  $\Psi$  which varies from zero at the voltammogram foot to its limiting value corresponding to the voltammogram plateau.

As it has been mentioned above the analytical expressions derived for the limiting current and the limiting electrostatic potential cover the most intriguing process carried out under the supporting electrolyte deficit, i.e. the charge reversal electrode processes. The interpretation of the self-enhancement effect of the faradaic current predicted for this class of electrode processes on the basis of the simplified theory has been extended by the predictions of the currently presented general theory that takes also varying content of supporting electrolyte into account. It turns out that one can distinguish the following ranges of  $\theta$  and  $\xi$  variables that define mathematical boundaries for the limiting current predicted for charge reversal processes (producing a univalent product):

1.  $D_P \ll D_S$  ( $\theta \rightarrow 0$ ),  $\xi < 1$  (supporting electrolyte deficit including its absence)

$$\frac{I^L}{I_d^L} \rightarrow \infty$$

2. any  $D_P$  and  $D_S$  (any  $\theta$ ),  $\xi \gg 1$  ( $\xi \rightarrow \infty$ , supporting electrolyte excess)

$$\frac{I^L}{I_d^L} \rightarrow 1$$

3.  $D_P \gg D_S$  ( $\theta \rightarrow \infty$ ), any  $\xi$

$$\frac{I^L}{I_d^L} \rightarrow 1 + |z| + 2\xi - 2\sqrt{\xi(\xi + |z|)}$$

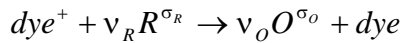
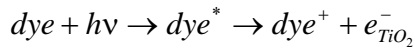
These interesting theoretical results have triggered an effort aimed at designing the redox system that undergoes the charge reversal electrode process.

### II.3 Mass transport coupled to the photoelectrochemical process in a mesoporous semiconductor layer and to the electrode process under the conditions of varying content of supporting electrolyte [H6]

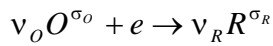
The inclusion of the electrode modified with the mesoporous semiconductor layer allowed one to understand better the effects of mixed diffusional and migrational transport of redox species driven by the photoelectrochemical phenomena. The dye-sensitized nanocrystalline TiO<sub>2</sub> solar cell (DSSC) served as a reference system. The model takes into account the presence of the bulk solution layer (containing a redox mediator and any level of supporting electrolyte) in contact with the mesoporous semiconductor anode, illumination from either side of the cell, and the attenuation of light due to its absorption by sensitizing molecules. The schematic representation of the cell and the operation principles are shown in Figure 2 and 3, respectively.

The sequence of the reactions occurring in the cell can be summarized as follows:

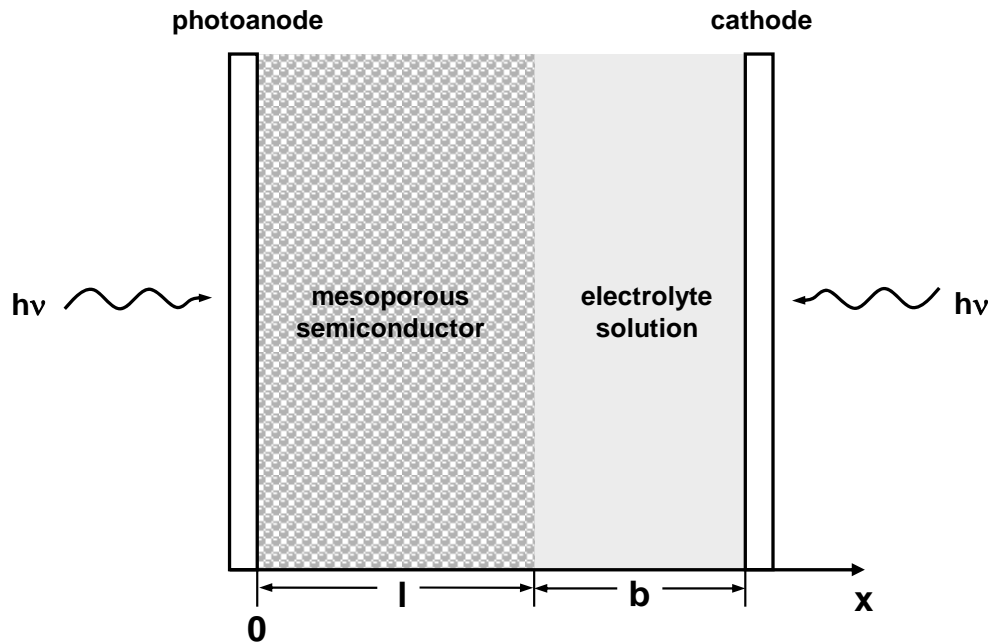
– anode (porous photoelectrode):



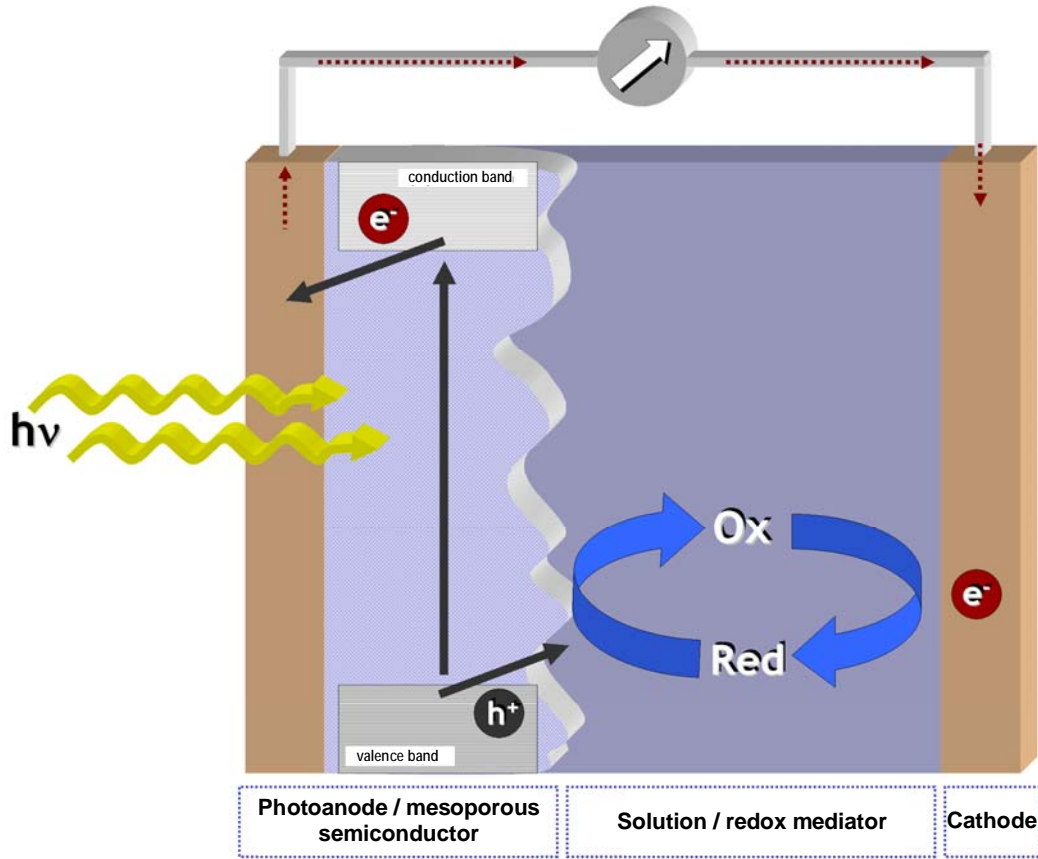
– cathode (counter electrode):



where  $\nu_R$ ,  $\nu_O$  and  $\sigma_R$ ,  $\sigma_O$  are the stoichiometric coefficients and charge numbers of the reduced and oxidized species of the redox mediator, respectively.



**Figure 2.** Schematic representation of a thin-layer photoelectrochemical cell employed for the theoretical modeling of diffusional and migrational transport.



**Figure 3.** Schematic representation of the operation principles of the photoelectrochemical cell.

The method developed for analytical solving the transport equations based on the quasi-potential transformation allowed one to model steady-state diffusional-migrational mass transport in a thin-layer cell involving a photoelectrochemically active semiconductor film electrode.

The transport equations written for each solute and referred to the current density delivered by the cell under the steady-state conditions constitute the system of nonlinear differential equations, which for the porous semiconductor film ( $X \in (0, l)$ ) and for the case of illumination from the photoelectrode side have the following form:

$$D_{Op} \frac{d}{dX} \left( \frac{dC_{Op}}{dX} + \sigma_o C_{Op} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) + r_o =$$

$$D_{Op} \frac{d}{dX} \left( \frac{dC_{Op}}{dX} + \sigma_o C_{Op} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) + \frac{v_o}{\varepsilon_p F} \left( \frac{j}{1 - e^{-A_\lambda}} \right) \varepsilon_\lambda C_{dye} e^{-\varepsilon_\lambda C_{dye} X} = 0$$

$$D_{Rp} \frac{d}{dX} \left( \frac{dC_{Rp}}{dX} + \sigma_r C_{Rp} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) - r_r =$$

$$D_{Rp} \frac{d}{dX} \left( \frac{dC_{Rp}}{dX} + \sigma_r C_{Rp} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) - \frac{v_r}{\varepsilon_p F} \left( \frac{j}{1 - e^{-A_\lambda}} \right) \varepsilon_\lambda C_{dye} e^{-\varepsilon_\lambda C_{dye} X} = 0$$

$$\frac{d}{dX} \left( \frac{dC_{Cp}}{dX} + C_{Cp} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) = 0$$

$$\frac{d}{dX} \left( \frac{dC_{Ap}}{dX} - C_{Ap} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) = 0$$

In the liquid layer ( $X \in (l, l+b)$ ) the concentrations of the species are only affected by the diffusional-migrational transport. Thus, under the steady-state conditions, the following transport equations apply:

$$\frac{d}{dX} \left( \frac{dC_{Os}}{dX} + \sigma_O C_{Os} \frac{F}{RT} \frac{d\Phi_s}{dX} \right) = 0$$

$$\frac{d}{dX} \left( \frac{dC_{Rs}}{dX} + \sigma_R C_{Rs} \frac{F}{RT} \frac{d\Phi_s}{dX} \right) = 0$$

$$\frac{d}{dX} \left( \frac{dC_{Cs}}{dX} + C_{Cs} \frac{F}{RT} \frac{d\Phi_s}{dX} \right) = 0$$

$$\frac{d}{dX} \left( \frac{dC_{As}}{dX} - C_{As} \frac{F}{RT} \frac{d\Phi_s}{dX} \right) = 0$$

where subscripts  $O, R, C, A, p, s$  correspond to the oxidized species, reduced species, electroinactive cations, electroinactive anions, porous layer, and liquid layer, respectively,  $r_O$  and  $r_R$  are the formation rate of species  $O$  and the consumption rate of species  $R$ , respectively,  $\varepsilon_\lambda$  is the extinction coefficient of the dye,  $C_{dye}$  represents the concentration of dye molecules,  $j$  is the current density delivered by the cell, the quantity  $(\varepsilon_\lambda C_{dye} l)$  is the absorbance,  $A_\lambda$ , of the semiconductor film of the thickness  $l$  at the specified light wavelength  $\lambda$ , and  $\Phi$  is the uncompensated electrostatic potential existing in the solution within the pores of the photoanode and in the bulk layer.

The set of the above eight equations contains 10 unknowns:  $C_{Op}(X)$ ,  $C_{Rp}(X)$ ,  $C_{Cp}(X)$ ,  $C_{Ap}(X)$ ,  $C_{Os}(X)$ ,  $C_{Rs}(X)$ ,  $C_{Cs}(X)$ ,  $C_{As}(X)$ ,  $\Phi_p(X)$ , and  $\Phi_s(X)$ . It is solvable by adding two extra equations, namely the electroneutrality relations

$$\sigma_O C_{Op} + \sigma_R C_{Rp} + C_{Cp} - C_{Ap} = 0 \quad X \in (0, l)$$

$$\sigma_O C_{Os} + \sigma_R C_{Rs} + C_{Cs} - C_{As} = 0 \quad X \in (l, l+b)$$

and the following boundary conditions:

$$X = 0: \quad \left( \frac{dC_{Op}}{dX} + \sigma_O C_{Op} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) = 0$$

$$\left( \frac{dC_{Rp}}{dX} + \sigma_R C_{Rp} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) = 0$$

$$\left( \frac{dC_{Cp}}{dX} + C_{Cp} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) = 0$$

$$\left( \frac{dC_{Ap}}{dX} - C_{Ap} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) = 0$$

$$X = l: \quad \varepsilon_p D_{Op} \left( \frac{dC_{Op}}{dX} + \sigma_O C_{Op} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) = D_{Os} \left( \frac{dC_{Os}}{dX} + \sigma_O C_{Os} \frac{F}{RT} \frac{d\Phi_s}{dX} \right)$$

$$\varepsilon_p D_{Rp} \left( \frac{dC_{Rp}}{dX} + \sigma_R C_{Rp} \frac{F}{RT} \frac{d\Phi_p}{dX} \right) = D_{Rs} \left( \frac{dC_{Rs}}{dX} + \sigma_R C_{Rs} \frac{F}{RT} \frac{d\Phi_s}{dX} \right)$$

$$\left( \frac{dC_{Cs}}{dX} + C_{Cs} \frac{F}{RT} \frac{d\Phi_s}{dX} \right) = 0$$

$$\left( \frac{dC_{As}}{dX} - C_{As} \frac{F}{RT} \frac{d\Phi_s}{dX} \right) = 0$$

$$C_{Op}(l) = C_{Os}(l)$$

$$C_{Rp}(l) = C_{Rs}(l)$$

$$C_{Cp}(l) = C_{Cs}(l)$$

$$C_{Ap}(l) = C_{As}(l)$$

$$\Phi_p(l) = \Phi_s(l)$$

and

$$\varepsilon_p \int_0^l C_{Op}(X) dX + \int_l^{l+b} C_{Os}(X) dx = (\varepsilon_p l + b) C_O^0$$

$$\varepsilon_p \int_0^l C_{Rp}(X) dX + \int_l^{l+b} C_{Rs}(X) dX = (\varepsilon_p l + b) C_R^0$$

$$\varepsilon_p \int_0^l C_{Cp}(X) dX + \int_l^{l+b} C_{Cs}(X) dX = (\varepsilon_p l + b) C_C^0$$

$$\varepsilon_p \int_0^l C_{Ap}(X) dX + \int_l^{l+b} C_{As}(X) dX = (\varepsilon_p l + b) C_A^0$$

where  $C_O^0$  and  $C_R^0$  are the initial concentrations of the species  $O$  and  $R$ , respectively,  $C_C^0$  and  $C_A^0$  are the total initial concentrations of electroinactive cationic and anionic species, respectively, and  $\varepsilon_p$  is the porosity coefficient of the semiconductor layer.

The proposed model provides analytical solutions of the transport equations (i.e., concentration profiles of each species present in the solution and electrostatic potential profiles) under steady-state conditions, for any level of ionic support and for redox mediators of various charge numbers. Using the general expressions derived one can summarize the solutions of the steady-state transport equations adjusted to the Grätzel cell (DSSC with the  $I_3^- / I^-$  system as the redox mediator). In this case, due to the reduction of triiodide ions, each mole of electrons initially injected into the semiconductor network is subsequently consumed at the cathode according to the reaction scheme  $\frac{1}{2} I_3^- + e \rightarrow \frac{3}{2} I^-$ . Assuming the illumination directed from the photoelectrode side, the electrostatic potential profiles take the form

$$\Psi_p(x) = -\ln \left[ 1 - \frac{J \left( \frac{3}{\theta_{Rp}} - \frac{1}{\theta_{Op}} \right) (1 - A_\lambda x - e^{-A_\lambda x})}{2\varepsilon_p (1 - e^{-A_\lambda}) A_\lambda \sum_i c_i(0)} \right]$$

for the porous film, and



$$\Psi_s(x) = \Psi_p(1) - \ln \left[ 1 - \frac{J \left( \frac{3}{\theta_{Rs}} - 1 \right) (1-x)}{2 \sum_i c_i(0) + \frac{J}{\varepsilon_p} \left( \frac{3}{\theta_{Rp}} - \frac{1}{\theta_{Op}} \right) \left( \frac{1}{1-e^{-A_\lambda}} - \frac{1}{A_\lambda} \right)} \right]$$

for the liquid layer, where

$$\sum_i c_i(0) = \sum_i c_i^0 - \frac{J}{2(\varepsilon_p + \beta)(1-e^{-A_\lambda})} \left( \frac{3}{\theta_{Rp}} - \frac{1}{\theta_{Op}} \right) \left[ \frac{1}{2} - \frac{1}{A_\lambda} + \frac{1-e^{-A_\lambda}}{A_\lambda^2} + \frac{\beta}{\varepsilon_p} \left( 1 - \frac{1-e^{-A_\lambda}}{A_\lambda} \right) \right] - \frac{J\beta^2}{4(\varepsilon_p + \beta)} \left( \frac{3}{\theta_{Rs}} - 1 \right)$$

The general relations describing concentration profiles of the electroinactive and redox ions are, in this case, simplified to the following equations

$$c_{Cp}(\Psi_p) = c_C(0)e^{-\Psi_p}$$

$$c_{Ap}(\Psi_p) = c_A(0)e^{\Psi_p}$$

$$c_{Op}(\Psi_p) = B_{1p}e^{\Psi_p} + B_{3p}e^{-\Psi_p}$$

$$c_{Rp}(\Psi_p) = B_{2p}e^{\Psi_p} + B_{5p}e^{-\Psi_p}$$

for the porous film, and

$$c_{Cs}(\Psi_s) = c_C(0)e^{-\Psi_s}$$

$$c_{As}(\Psi_s) = c_A(0)e^{\Psi_s}$$

$$c_{Os}(\Psi_s) = B_{1s}e^{\Psi_s} + B_{3s}e^{-\Psi_s}$$

$$c_{Rs}(\Psi_s) = B_{2s}e^{\Psi_s} + B_{5s}e^{-\Psi_s}$$

for the liquid layer, where the  $B$  coefficients are determined using surface concentrations of

supporting ions at  $x = 0$ ,  $x = \frac{X}{l}$ ,  $\beta = \frac{b}{l}$ ,  $c_{ip} = \frac{C_{ip}}{C_O^0}$  ( $i = O, R, C, A$ ),  $c_{is} = \frac{C_{is}}{C_O^0}$  ( $i = O, R, C, A$ ),

$$\theta_{ip} = \frac{D_{ip}}{D_{Os}} \quad (i = O, R), \quad \theta_{Rs} = \frac{D_{Rs}}{D_{Os}}, \quad \Psi = \frac{F}{RT}(\Phi - \Phi(0)), \quad J = j \frac{l}{FD_{Os}c_O^0}.$$

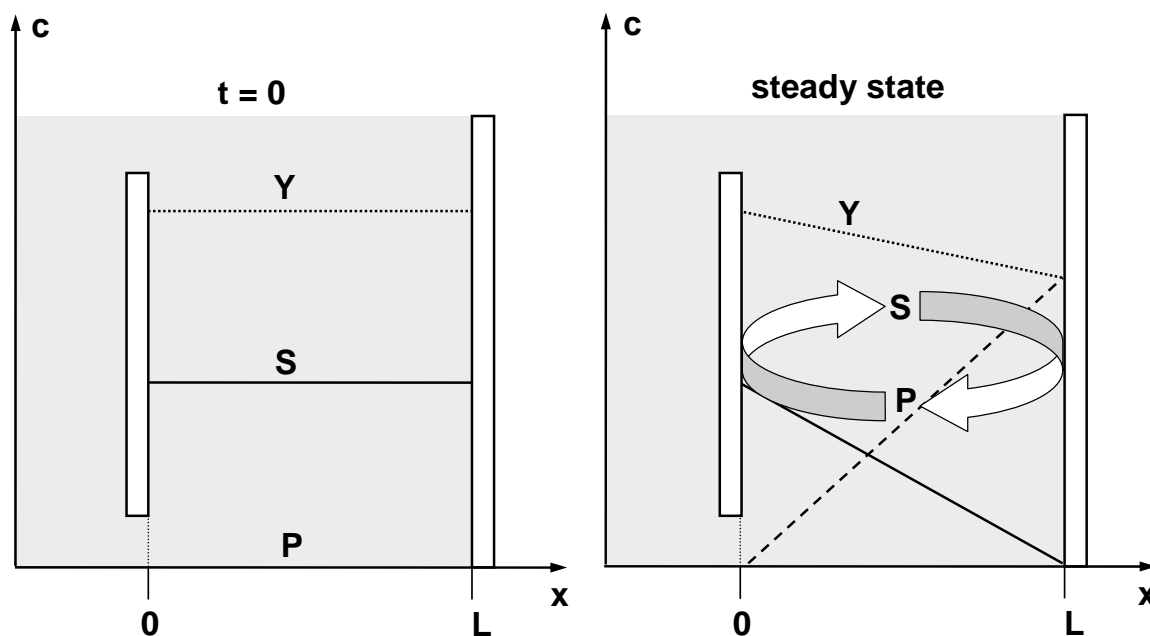
The proposed theoretical model provides detailed analysis of the cell design parameters and operational conditions that affect diffusion-migration driven mass transport in the dye-sensitized, mesoporous semiconductor-based, photoelectrochemical cells under steady-state conditions. The derived expressions predict the extent to which the mass transport is influenced by various parameters characterizing both the redox mediator (charge numbers, diffusion coefficients, initial concentrations of the redox species) and the cell design (porous layer thickness and its porosity, solution layer thickness, direction of the electrode illumination, type and the amount of the supporting electrolyte). Additionally, it was found that the mass transport limitations arise above a certain illumination level of the cell and manifest themselves as a deviation from a linear dependence of the photocurrent upon light intensity.

The derivation scheme can also be easily adapted for the investigation of transport processes driven by diffusion and migration in other types of the photoelectrochemical systems, e.g. in the cells where the porous semiconductor film electrode is used to carry photocatalytic reactions under the band-gap illumination. It can also be used for studying mass transport through a porous structure in a thin-layer cell involving electrochemically inactive porous film (e.g. polymeric gel) deposited on the electrode surface. In both cases, to be able to take advantage of the developed approach one needs to re-formulate appropriately the boundary conditions coupled to the set of transport equations.

#### II.4 Thin and ultra-thin layer dual electrode system in the absence of supporting electrolyte [H10]

As it has been mentioned in the previous sections the absence of supporting electrolyte leads to a specific great variety in electrode responses when the charge numbers and diffusion coefficients of electroactive species vary. The variability in the voltammetric behavior of the redox species may be further increased after diminishing the size of- or the distance between the working electrodes to the nanometer range.

If the solution containing a redox species is placed between two closely-spaced plane electrodes (separated by a distance  $l$ ) oriented parallel to each other, and both electrodes are independently polarized, then the mass transport will take place in the limited linear space and the steady-state conditions will be easily attainable. The schematic representation of the cell along with the initial and steady-state concentration profiles is presented in Figure 4. In such the electrochemical cell the product of the electrooxidation at one electrode is transported to- and re-electroreduced at the other electrode (communicating electrodes).



**Figure 4.** Schematic representation of a thin-layer electrochemical cell bounded on both sides by electrodes (communicating electrode system). The initial ( $t = 0$ ) and steady-state limiting concentration profiles of all species are included. It is assumed that the electrode placed at  $X = 0$  acts as cathode and anode is placed at  $X = l$ .

In the absence of supporting electrolyte the set of the steady-state transport equations, after applying the normalization rules and quasi-potential transformation, takes the following form:

$$\left( \frac{dc_S}{d\Psi} + z_S c_S \right) \frac{d\Psi}{dx} = -i$$

$$\left( \frac{dc_P}{d\Psi} + z_P c_P \right) \frac{d\Psi}{dx} = \frac{i}{\theta}$$

$$\left( \frac{dc_Y}{d\Psi} + z_Y c_Y \right) \frac{d\Psi}{dx} = 0$$

The system of equations is coupled to the electroneutrality principle and in the same time to the mass conservation law:

$$\int_{x=0}^{x=1} (c_S + c_P + c_Y) dx = \left( 1 - \frac{z_S}{z_Y} \right)$$

where subscripts  $S$ ,  $P$  and  $Y$  correspond to the substrate, the product and substrate's counterion, respectively,  $c_i = \frac{C_i}{C_S^0}$  ( $i = S, P, Y$ ),  $\theta = \frac{D_P}{D_S}$ ,  $x = \frac{X}{l}$  ( $x \in [0,1]$ ),

$\Psi = \frac{F}{RT} (\Phi - \Phi(X=0))$ ,  $i = \frac{I}{nFAD_S C_S^0} l$ ,  $A$  is the electrode surface, and  $C_S^0$  denotes the initial concentration of the electroactive species for the anodic electrode process.

The integration of the transport equations followed the procedure described in previous sections. Similarly to the previous models, the obtained analytical solutions allowed derivation of the analytical expressions for the limiting electrostatic potential and the limiting faradaic current. Interestingly, the expression for the limiting electrostatic potential,  $\Psi^L$ , at the interface is identical to that derived for the semi-infinite diffusional-migrational transport to a hemispherical microelectrode in the absence of supporting electrolyte. The corresponding expression for the limiting current normalized with respect to the purely diffusional response,  $i_d^L$ , is identical to its equivalent derived for the semi-infinite diffusional-migrational transport to a hemispherical microelectrode if  $z_S z_P (\theta - 1) = 0$ . The latter is satisfied when either  $\theta$  is equal to 1 (equal diffusion coefficients of electroactive species, any  $z_S, z_P, z_S \neq z_P$ ) or  $z_S$  is zero (uncharged substrate, any  $\theta$  and  $z_P$ , and  $z_S \neq z_P$ ) or  $z_P$  is zero (uncharged product, any  $\theta$  and  $z_S$ , and  $z_P \neq z_S$ ). If both electroactive species bear charge (i.e. for  $z_S z_P (\theta - 1) \neq 0$  and  $\text{sgn}(z_S) = \text{sgn}(z_P)$ ) a specific relation between  $i^L / i_d^L$  and  $\theta$  is established for various  $z_S, z_P, z_X$  values

$$\frac{i^L}{i_d^L} = \frac{\theta + 1}{\theta - 1} \left[ \frac{z_P (z_Y - z_S)^2 + z_S (z_P - z_Y) (z_Y - z_S) e^{-z_Y \Psi^L}}{z_P z_Y (z_Y - z_S) + z_S z_Y (z_Y - z_P) e^{-z_Y \Psi^L}} \right]$$

where  $i_d^L$  is the dimensionless steady-state limiting current under the conditions of excess supporting electrolyte (purely diffusional conditions) given by

$$i_d^L = \frac{2\theta}{\theta + 1}$$

The theoretical modeling revealed high sensitivity of the thin-layer electrode system response to the diffusion coefficients diversity. It is particularly pronounced for the charge reversal processes: the  $\theta$  - dependence of the limiting current “blows up” at  $\theta = 1$  where the limiting conditions can not be reached and the transport is purely migrational.

Finally, the theory allowed one to examine quantitatively the limitation of the derived expressions due to the application of the electroneutrality condition at any point in the system. The electroneutrality approximation in the mass transport modeling associated with the electron exchange implies that the electric field resulting from the flow of current through a

solution is not big enough to induce the charge accumulation at any point in the solution. This assumption is generally valid if the electrical double layer occupies an insignificant fraction of the transport depletion layer. This may become questionable when the distance between the electrodes tends to nanometer range. The electrode system modeled in this work gave us the opportunity to test the validity of the electroneutrality condition. To perform testing the derived general expression for the electrostatic potential distribution was introduced to the Poisson equation, which in dimensionless form is given by:

$$-\left(\frac{\varepsilon\varepsilon_0RT}{F^2C_S^0l^2}\right)\frac{d^2\Psi}{dx^2} = z_S c_S + z_P c_P + z_Y c_Y \equiv \rho_{exc}$$

where  $\varepsilon$  is the relative dielectric constant,  $\varepsilon_0$  is the permittivity of vacuum, and  $\rho_{exc}$  is the local net charge density in the solution. The factor  $\varepsilon\varepsilon_0RT/F^2$  is fixed for room temperature ( $T = 298$  K) and for aqueous solutions ( $\varepsilon = 78$ ).

The implicit differentiation of the distance dependence of the electrostatic potential derived with the electroneutrality approximation yields the estimate of the magnitude of the error that appeared as a result of employing the electroneutrality condition rather than the Poisson equation. This estimate is quantified using the excessive charge density denoted by  $\rho_{exc}$ .

It was found that the departure from the electroneutrality diminishes with the increase in the distance between the electrodes. For a 100-nm separation of electrodes and comparable diffusion coefficients of the redox species,  $\rho_{exc}$  does not exceed 1% of  $C_S^0$ . For the electrode processes with charge sign retention (for which the limiting conditions can be reached) the error  $\rho_{exc}$  does not exceed 10% of  $C_S^0$  down to 60-nm gap between the electrodes for the entire  $\theta$  range examined (0.2 – 5.0). The calculations indicated also a strong dependence of  $\rho_{exc}$  with respect to  $\theta$ . However, the direction of this dependence is a function of the type of the electrode process.

Two theoretical consequences of the performed analysis are worth noting. It turns out that electroneutrality will hold unquestionable at any point in the solution if  $\theta$  is equal to  $z_P / z_S$ . This specific value of  $\theta$  makes the uncompensated electrostatic field vanish even in the absence of supporting electrolyte. Also, the electroneutrality is expected to be satisfied at any point if the electrode process is of charge reversal type and the redox species diffusivities are equal. In this case the transport is totally driven to preserve electroneutrality.

The theoretical predictions derived for ultra-thin layer dual electrode system provide quantitative characteristics of the redox cycling process affected by the migrational contribution. The results may be of great significance for the extension of applicability of many devices utilizing redox cycling, including the electrochemical scanning microscopy in low-supported media.

Additionally, by decreasing the distance between the electrodes to the nanometer range it may be possible to perform electrochemical detection of individual redox-active molecules affected by migration. This project has been already initiated in cooperation with Prof. S.G. Lemay group (University of Twente, The Netherlands).

### III. Methods for the determination of diffusion coefficients of the electrode process substrate and product [H1, H2]

There are some evident advantageous features in the evaluation of diffusion coefficients in the low-supported (a small ratio of bulk concentrations of supporting electrolyte and substrate) media. The determined values of diffusion coefficients are not affected by the ionic strength. This makes the obtained results comparable to those obtained with non-electrochemical methods, such as light scattering spectroscopy, pulsed-field-gradient spin-echo NMR

spectroscopy and radioactive tracer methods which are always carried out with no deliberately added inert electrolyte. It should be particularly useful to study the transport properties of the redox species in the systems containing inert electrolytes at unknown concentrations or in the systems where the introduction of excess supporting electrolyte is impossible or not recommended, e.g. in low-polarity solvents, solid materials, environmental samples etc.

The electrochemical evaluation of diffusion coefficients is usually based on the use of the transient- and the steady-state techniques, such as chronoamperometry, chronocoulometry, voltammetry, and chronopotentiometry. Commonly, the diffusion coefficients of the substrates are determined. For this purpose the knowledge of the electrode area, the number of electrons transferred per molecule, and the bulk concentration of the substrate is required. Additionally, the system must contain excess supporting electrolyte to eliminate the migrational contribution to the transport of the species studied.

The numerical modeling of diffusional and migrational transport, being a main theme in my Ph. D. studies, resulted in development of a method for the determination of diffusion coefficients of both: the substrate ( $D_S$ ) and the product ( $D_P$ ) of an electrode process for any level of ionic support, including the absence and the excess of supporting ions. The new method employs double potential step chronoamperometry and requires the knowledge of the radius of microelectrode prior to the chronoamperometric experiment and the employment of the common tools for the linear regression analysis.

It has been shown that double potential step chronoamperometry which, in fact, consists of two coupled transient experiments, may provide the complete information on the transport properties of the studied redox couple, irrespective of the level of ionic support present in the system. The diffusion coefficients of both: the substrate and the product can be evaluated sequentially from the appropriate parts of the double-potential step experiment at microelectrodes of various geometries [H1]. The magnitude of the normalized chronoamperometric current of the first step depends on the  $D_S$  value. Assuming that a disk microelectrode is applied for the measurements, the latter can be determined using the following formula:

$$D_S = \frac{4r_{e,d}^2}{\pi^3} \left( \frac{1}{a} - \frac{1}{\sqrt{t_g}} \right)^2$$

where  $r_{e,d}$  is the radius of the disk microelectrode,  $t_g$  denotes the duration time of the generating step (the duration of the first potential pulse; due to the double-layer charging effects and the large variation of the uncompensated electrostatic potential, particularly for the severe deficit of supporting electrolyte,  $t_g$  should not be less than 0.5 ms ( $t_g^{lim}$ )), and  $a$  is the slope of the linearized dependence of  $I^L(\xi, t) / I^L(\xi, t_g)$  vs.  $1/\sqrt{t}$ , i.e.

$$\frac{I^L(\xi, t)}{I^L(\xi, t_g)} = a \frac{1}{\sqrt{t}} + b + O(t^{-3/2}) \quad t_g^{lim} < t \leq t_g$$

The limiting chronoamperometric current of the generating step  $I^L$  is normalized with respect to the value measured at  $t_g$  for any support ratio,  $\xi$ .

The magnitude of the normalized chronoamperometric current of the second (reverse) step in the double potential step chronoamperometric experiment is controlled by both  $D_S$  and  $D_P$  values. Having the substrate diffusivity  $D_S$  determined from the first step one can use it for the evaluation of  $D_P$  from the second step using the following formula:

$$D_p = \frac{1}{a^2} \left( \frac{\pi\sqrt{\pi}}{2r_{e,d}} + \frac{1}{\sqrt{D_s t_g}} \right)^{-2}$$

where  $a$  is the slope of the linearized dependence of  $I_r(\xi, t) / I^L(\xi, t_g)$  vs.  $1/\sqrt{t-t_g}$ , i.e.

$$\frac{I_r(\xi, t)}{I^L(\xi, t_g)} = a \frac{1}{\sqrt{t-t_g}} - \frac{a}{\sqrt{t_g}} + O(t-t_g)$$

where  $I_r$  is the chronoamperometric current measured for the reverse potential step, and is made dimensionless with respect to the value of the chronoamperometric current measured at  $t_g$  for any support ratio,  $\xi$ .

An alternative approach that enables evaluation of the diffusion coefficient of the electrode process product originated from the derived theory of the steady-state mass transport in the systems with no added supporting electrolyte [H2]. It was found that the expression relating the limiting current  $I^L$  and the  $\theta$  parameter ( $D_p / D_s$ ) can be linearized for relatively wide range of the  $\theta$  values and can be represented as

$$\frac{I^L}{I_d^L} = \frac{I_1^L}{I_d^L} + a \ln \left( \frac{D_p}{D_s} \right)$$

where  $I_1^L$  is the predicted limiting current calculated for a supporting electrolyte-free solution with the assumption of equal diffusion coefficients of the substrate and the product, and the  $a$  coefficient is a function of  $z_s$ ,  $z_p$ , and  $z_x$  generated by the Taylor expansion. The numeric values of  $I_1^L / I_d^L$  and  $a$  for a monovalent counterion and for various  $z_s$  and  $z_p$  combinations can be easily tabulated.

The convenient form of the linear dependence of  $I^L$  vs.  $\ln(D_p / D_s)$  and simple experimental realization of the measurement procedure make the determination of the product diffusion coefficient straightforward. To apply this approach one needs to record the steady-state voltammograms at a microelectrode for an examined redox species in systems containing no- and sufficient excess of supporting electrolyte. In the latter case, the steady-state voltammetric response is a direct source of the information on the substrate diffusivity, and is given by the well-know formula:

$$I_d^L = gnFD_s C_s^b r_e$$

where  $g$  is the geometric coefficient of the microelectrode employed in the measurements.

Both approaches developed for the determination of diffusion coefficients were examined experimentally with potassium hexacyanoferrate (II) and the charged- and the uncharged derivatives of ferrocene (ferrocene ( $\text{Fe}(\text{C}_5\text{H}_5)_2$ ), 1,1'-ferrocenedimethanol ( $\text{Fe}(\text{C}_5\text{H}_4)_2(\text{CH}_2\text{OH})_2$ ), sodium ferroceneacetate ( $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)(\text{CH}_2\text{COO}^-) \text{Na}^+$ ), and ferrocenylmethyltrimethylammonium hexafluorophosphate ( $\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_4)(\text{CH}_2\text{N}(\text{CH}_3)_3)^+ \text{PF}_6^-$ )) in several solvents.

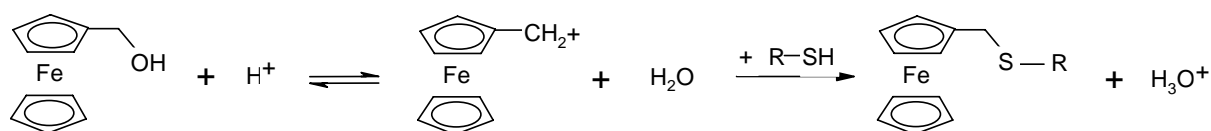
It is worth noting that both (chronoamperometric and steady-state voltammetric) approaches produce statistically comparable results for the product and the substrate diffusivities.

#### **IV. Design and custom synthesis of new redox systems based on ferrocene unit dedicated to the validation of the theoretical predictions [H3, H4, H7, H8]**

Validation of the theoretical models and experimental verification of the methods for the determination of diffusion coefficients of the substrate and the product of the electrode process were performed using the experimental results obtained for the selected redox species.

The redox systems involved commercially available ferrocene derivatives and self-designed and synthesized ionized ferrocene derivatives to better expose specific effects (either enhancement or depression) resulting from the migrational contribution to the mass transport. Inserting the polar groups to the ferrocene moiety(ies) enabled one to study the migrational transport of differently ionized but similar in geometry molecules. On the other hand, the presence of the ferrocene center (which is known as a fast-electron-exchange molecule at electrodes of the micrometer dimension) was supposed to reduce, at least to some extent, the limitations in electron-transfer kinetics. In addition to this, the derivatization of ferrocene unit made the whole system soluble in water. Therefore, such the redox systems gained an extra advantage to probe redox processes that occur in biological systems. The synthesis followed a path established by us in a cooperation with dr. B. Misterkiewicz (University of Technology and Humanities in Radom, Poland).

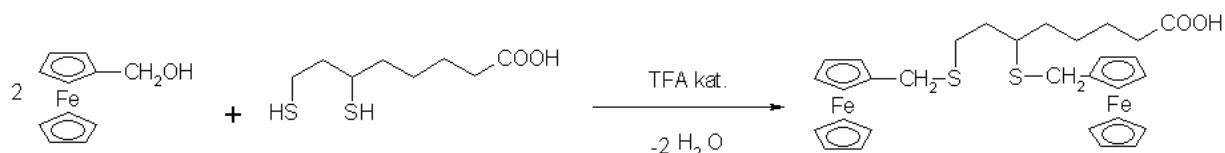
The common reaction path used for the synthesis of the series of new ferrocene derivatives summarizes schematically the sketch below



where  $R$  can also represent another mercapto-ferrocenyl group.

The key factor in the proposed synthetic procedure was the proper choice of the catalyst. Trifluoroacetic acid (TFA) is commonly used for that purpose. However, difficulty in its removal after the reaction is completed is the most limiting feature of the reaction scheme. According to our studies, replacing TFA with Nafion resulted in an increased reaction yield and is free of the limitations mentioned above.

The most intriguing effects are predicted for the processes that undergo with the reversal of the sign of electroactive-species charge numbers (the charge number of the electrode process product has the opposite sign to that of the substrate). Therefore, the experimental work was initiated with the design of a ferrocene derivative (sodium (6,8-diferrocenylmethylthio)octanoate) that was expected to possess such the properties. A synthetic work aimed at obtaining sodium (6,8-diferrocenylmethylthio)octanoate can be represented by the following schematic reaction sketch

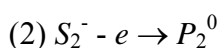
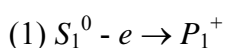


A 2-e oxidation of the negatively charged diferrocene derivative (6,8-diferrocenylmethylthio)octanoate can serve as an example of the charge reversal process. According to the predictions of the theoretical models of microelectrode response, the faradaic current for this class of electrode processes increases limitlessly as supporting electrolyte is totally eliminated from the system. As a result, instead of typical wave-shaped voltammograms (with plateau), ramp-shaped ones are predicted. This behavior is a direct consequence of the preservation of the electroneutrality principle which is incorporated into the theoretical models, since the substrate of the electrode process serves as the counterion to

the product of the electrode process. Ramp-shaped voltammograms were not recorded for the examined species but a strong enhancement in the transport rate was clearly observed (the experimental voltammetric waves were significantly amplified compared to diffusional ones) [H4]. Several factors might induce destruction of the ramp-shaped voltammograms and reversing them to the typical waves with plateaus. Among the most probable for this compound one may list: a homogeneous reaction leading to the generation of uncharged species in the form of an ion pair, a hardly soluble salt or a product of the comproportionation reaction, and the presence of an unspecified amount of ionic impurities introduced to the solution which act as supporting ions.

An improved synthetic work aimed at obtaining analogous diferrocene compound (i.e., sodium salt of *S,S*-diferrocenylmethyl-2,3-dimercapto-1-propanesulfonic acid) is now under consideration. In the process of molecular designing of charge-reversal representative a shorter linkage between the ferrocene units and the introduction of the sulfonic group (making the whole molecule negatively charged) have been assumed. This work has been already initiated.

Another practical realization, that was supposed to mimic the transport behavior observed for the redox species undergoing the charge reversal electrode processes, involved parallel electrode processes of two redox systems in the absence of supporting electrolyte [H3]. The pairs of ferrocene derivatives were selected for the examination in such a way that one substrate was neutral (1,1' – ferrocenedimethanol) and the other one – ionic (ferroceneacetate, ferrocenesulfonate). The formal redox potentials and the diffusion coefficients of such the redox species were sufficiently similar to avoid the effect of nonadditive voltammetric currents. In the absence of supporting electrolyte the ionic substrate served as the counterion for the product of the electrooxidation of the neutral redox compound. To preserve the electroneutrality in the depletion layer the ionic product attracted electrostatically the oppositely charged substrate of the parallel process. This resulted in a significant enhancement of the transport of the ionic substrate and, consequently, an increase in the resulting current compared to a situation, where ionic substrate is present alone in a solution with no supporting electrolyte. Schematically the parallel processes of the examined ferrocene derivatives can be represented by the following sequence of the electrode reactions:



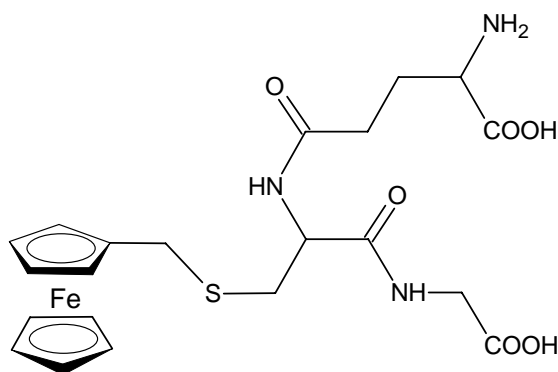
where *S* and *P* symbolize the substrate and the product of the electrode process.

By replacing a negatively charged ferrocene derivative with a positively charged derivative (ferrocenylmethyltrimethylammonium hexafluorophosphate) a significant depression of the transport of ionic substrate took place. The corresponding voltammetric response is much lower compared to a situation where the ionic substrate is present alone in a supporting-electrolyte free system.

Finally, the research work presented in a series of papers [H7, H8] was focused on investigation of the mass transport of two biologically-active thiols (called biothiols: tripeptide glutathione and L-cysteine) derivatized with the ferrocenyl group. The studies were performed in aqueous solutions under the conditions of varying content of supporting electrolyte and at different pH values. Due to the ability of thiols to undergo redox reactions, these compounds are found to be important water-phase antioxidants that provide protection for the mitochondria against oxygen radicals. By applying the synthetic procedure described above one was able to attach an electroactive group, such as ferrocenyl group, to a molecule of biologically active compound. This allowed the steady-state voltammetry at microelectrodes to be applied to the transport studies of the obtained new ferrocene



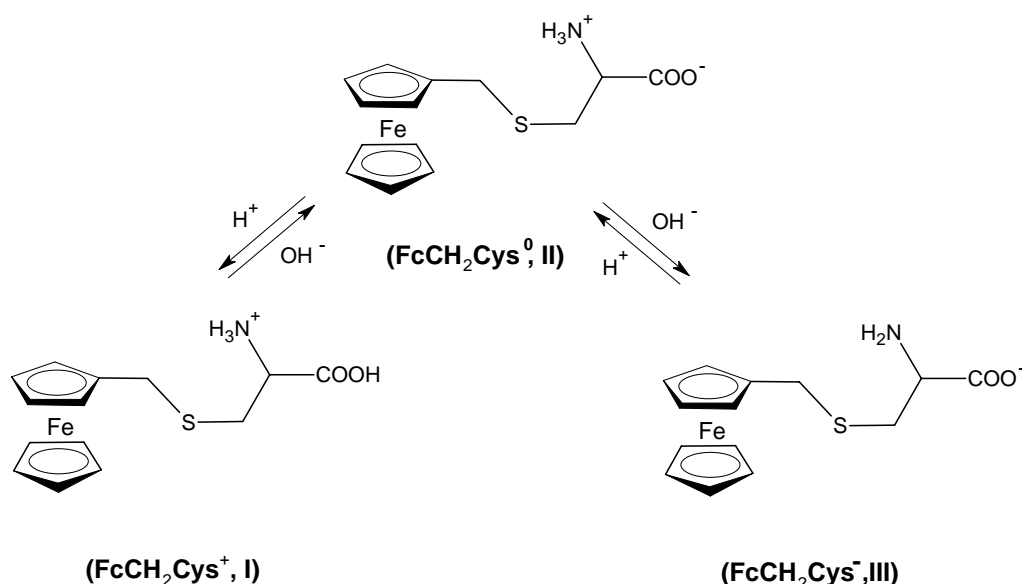
derivatives: S-ferrocenylmethyl-L-glutathione (Figure 5) [H7] and S-ferrocenylmethyl-L-cysteine (Figure 6) [H8].



**Figure 5.** Schematic structure of S-ferrocenylmethyl-L-glutathione.

By measuring the transport-limited current due to the oxidation of the ferrocene group at varying content of supporting ions it was possible to trace the transport of such molecules driven by migration and diffusion. It was demonstrated that the strong dependence of the limiting voltammetric current of charged species on support ratio and the ratio of diffusion coefficients of the electrode process product and the substrate, predicted by the developed theory, can be used for diagnosis of possible structural changes of the substrate upon reduction / oxidation. The latter is especially vital for the peptide / enzyme functionality, since the changes in the structure of such the biological systems may affect their activity [H7]. This type of the structural change in the electrode reaction systems could not be detected under the purely diffusional conditions (in the presence of excess supporting electrolyte).

It is also worth noting that the net charge number of both redox biothiol derivatives is an exclusive function of the solution pH. By varying the pH conditions one could obtain samples containing differently ionized forms of these compound. This was particularly evident for L-cysteine derivative for which one could study the transport behavior of a monovalent cation via a neutral form (zwitterion) to a monovalent anion (Figure 6) [H8]. Under the conditions of low ionic support the mass transport of these forms and, consequently, their concentration profiles, are differently affected by the migrational contribution. The concentration distribution is another important factor affecting biological activity of biothiols.



**Figure 6.** Schematic structures of S-ferrocenylmethyl-L-cysteine forms existing in aqueous solution.

Recently, new biologically active derivatives of ferrocene that take advantage of the fast electron transfer and moderate toxicity of ferrocene moiety for human organism, are being developed for the therapeutic applications.

The results of the studies on diffusional and migrational transport to microelectrodes and their implication for electroanalysis were summarized in the chapter of Encyclopedia of Analytical Chemistry [H9].

## V. Summary

The most important achievements of the research work presented in the series of papers setting the basis for the habilitation include:

- the development of the integration scheme for analytical solving the mixed diffusional and migrational transport equations under the steady-state conditions with no restriction on the magnitudes of diffusion coefficients of the substrate and the product of an electrode process [H2, H5];
- the theories of the mixed diffusional and migrational transport in various electrochemical systems:
  - semi-infinite transport to a hemispherical working microelectrode in the absence [H2] and at varying content of supporting electrolytes [H5];
  - dye-sensitized solar cell (mass transport in the limited field of the porous layer being in contact with the solution bulk containing varying content of supporting electrolyte) [H6];
  - thin and ultra-thin layer dual electrode system (nanogap devices with the mass transport realized in the limited space in the absence of supporting electrolyte, and testing the validity of the electroneutrality approximation) [H10]
- the development and practical realization of new methods for the determination of diffusion coefficients of the substrate and the product of the electrode process at microelectrodes under the conditions of varying ionic support (the double-potential

- step chronoamperometry method [H1] and the steady-state voltammetry method [H2]);
- the experimental verification of the theoretical predictions using the self-designed and synthesized (in cooperation) ferrocene-based redox systems that exhibit desired transport properties
    - sodium (6,8-diferrocenylmethylthio)octanoate (its electrooxidation is an exemplification of the charge reversal process for which the theory predicts self-enhancement of the faradaic current, if supporting electrolyte is eliminated from the system) [H4];
    - S-ferrocenylmethyl-L-glutathione [H7] and S-ferrocenylmethyl-L-cysteine [H8] (detection of changes in the concentration distribution of biologically active molecules driven by migration and diffusion and their possible structural changes upon reduction / oxidation in a function of the solution pH and the supporting electrolyte level);
  - generalization of the theoretical fundamentals of electroanalytical techniques [H9].

## 5. List of other scientific achievements

### 5. A Summary of the indices of scientific achievements (Web of Science, June 03, 2013)

Total number of publications (articles in journals included In Thomson Reuters Journal Citation Reports): 23

Total numbers of books and book chapters: 2

Total IF: 82.268 (3.577/publ.)

Total number of citations: 263 (11.43/publ.)

Total number of citation without self-citations: 211

Hirsch index  $h = 11$

Three publications accepted for publication (including H10) are not indexed. Total IF of these three publications: 13.763.

### 5. B List of other scientific publications (not included in the achievement listed in sect. 4). Articles in journals included In Thomson Reuters Journal Citation Reports

#### I. List of publications before the Ph. D. degree

	Authors, title, journal, volume, year, pages	IF	Number of citations
1	<b>W. Hyk</b> , M. Pałys, Z. Stojek “Migrational Chronoamperometry of Uncharged Substrates. Influence of Electron Transfer Rate” <i>J. Electroanal. Chem.</i> , 415 (1996) 13-22.	2.905	36

2	<b>W. Hyk</b> , Z. Stojek “Chronoamperometry of Uncharged Species under the Conditions of Deficiency of Supporting Electrolyte: Experiment vs. Theory” <i>J. Electroanal. Chem.</i> 422 (1997) 179-184.	2.905	23
3	M. Donten, <b>W. Hyk</b> , M. Ciszowska, Z. Stojek “Electrooxidation of Ammonia and Simple Amines at Titanium Electrodes Modified with a Mixture of Ruthenium and Titanium Dioxides” <i>Electroanalysis</i> , 9 (1997) 751-754.	2.872	11
4	<b>W. Hyk</b> , Z. Stojek “Migrational Chronoamperometry for Various Reaction Stoichiometries and a Variety of Types of Supporting Electrolyte” <i>J. Electroanal. Chem.</i> , 439 (1997) 81-88.	2.905	14
5	<b>W. Hyk</b> , Z. Stojek “Physicochemical Consequences of Generating a Thin Layer of Ionic Liquid at Microelectrode Surface in Undiluted Redox Liquid” <i>J. Phys. Chem. B</i> , 102 (1998) 577-584.	3.696	20
6	<b>W. Hyk</b> , Z. Stojek “Reverse Pulse Voltammetry and Double Potential Step Chronoamperometry as Useful Tools for Characterization of Electroactive Systems under the Conditions of Mixed Diffusional and Migrational Transport” <i>Anal. Chem.</i> , 70 (1998) 5237-5243.	5.856	4
7	<b>W. Hyk</b> , M. Ciszowska “Studies of Transport Phenomena and Electrostatic Interactions in Polyacrylate Gels” <i>J. Phys. Chem. B</i> , 103 (1999) 6466-6474.	3.696	23

IF and number of citations are based on the Web of Science and Journal Citation Reports databases (June 03, 2013).

I started my first research project in the last years of graduate studies at the Faculty of Chemistry, University of Warsaw in Laboratory of Theory and Applications of Electrodes. The main goal of my research work was the numerical modeling (digital simulation) of the diffusional transport affected by migration and convection for the selected classes of electrode processes in various media (aqueous solutions, undiluted redox liquids, polyelectrolytes, polymeric gels). The main achievement was the development of the general numerical model of the mass transport dynamics (which is governed by Fick's law) driven by the electrode process of an uncharged redox species at varying content of supporting electrolyte. The kinetics of the heterogeneous electron transfer was also taken into account.

All calculations were performed using the self-made computer applications written in C/C++ programming language.

Much of my papers published at this stage of research set the basis for the Ph. D. thesis entitled “Diffusional and Migrational Transport of Molecules and Ions to Microelectrodes in Various Media”, defended in December 1999.

## II. List of publications after the Ph. D. degree

	Authors, title, journal, volume, year, pages	IF	Number of citations
1	<b>W. Hyk</b> , M. Ciszowska “Voltammetric Studies of Transport Properties of Poly(N-isopropylacrylamide-co-Acrylic Acid) Gels Swollen by Methanol” <i>J. Electrochem. Soc.</i> , 147 (2000) 2268-2272.	2.590	9
W. Hyk (80%): preparation of gel samples; chronoamperometric and voltammetric measurements; calculations; data interpretation; concept of the manuscript layout and its preparation (text, tables, figures).			
2	<b>W. Hyk*</b> , K. Caban, M. Donten, Z. Stojek „Properties of Microlayers of Ionic Liquids Generated at Microelectrode Surface in Undiluted Redox Liquids. Part II” <i>J. Phys. Chem. B</i> , 105 (2001) 6943-6949.	3.696	9
W. Hyk (60%): participation in voltammetric measurements; analysis of the experimental data; determination of diffusion coefficients; interpretation of the obtained results; participation in the manuscript preparation (text, tables, figures); corresponding author.			
3	K. Caban, <b>W. Hyk</b> , M. Donten, Z. Stojek „Influence of Gravitation on Steady-State Currents of Undiluted Alcohols at Microelectrodes” <i>Chem. Anal.</i> , 46 (2001) 813-822.	0.520	4
W. Hyk (30%): participation in voltammetric measurements; analysis of the experimental data; participation in the manuscript preparation.			
4	<b>W. Hyk</b> , M. Ciszowska “Preparation and Characterization of Poly(N-isopropylacrylamide-co-Acrylic Acid) Gels Swollen by Non – Aqueous Solvents: Alcohols” <i>J. Phys. Chem. B</i> , 106 (2002) 11469-11473.	3.696	12
W. Hyk (80%): preparation of gel samples; chronoamperometric and voltammetric measurements; calculations; data interpretation; concept of the manuscript layout and its preparation (text, tables, figures).			
5	<b>W. Hyk*</b> , M. Karbarz, Z. Stojek, M. Ciszowska „Efficiency of Solute Release from Thermoresponsive Poly(N-isopropylacrylamide) Gels: Electrochemical Studies” <i>J. Phys. Chem. B</i> , 108 (2004) 864-868.	3.696	15
W. Hyk (60%): derivation of the theoretical model; participation in the preparation of gel samples; participation in voltammetric and conductometric measurements; calculations; interpretation of the obtained results; concept of the manuscript layout and its preparation (text, tables, figures); corresponding author.			
6	<b>W. Hyk</b> , M. Masiak, Z. Stojek, M. Ciszowska „Diffusion of Uncharged Probe Reveals Structural Changes in Polyacids Initiated by Their Neutralization. Poly(Acrylic Acids)” <i>J. Phys. Chem. B</i> , 109 (2005) 4425-4430.	3.696	4

W. Hyk (60%): development of the theoretical model; participation in voltammetric measurements; analysis of the experimental data; interpretation of the obtained results; participation in the manuscript preparation (text, tables, figures).

7	M. Masiak, <b>W. Hyk</b> , Z. Stojek, M. Ciszowska “Structural Changes of Polyacids Initiated by Their Neutralization with Various Alkali Metal Hydroxides. Diffusion Studies in Poly(Acrylic Acid)s” <i>J. Phys. Chem. B</i> , 111 (2007) 11194-11200.	3.696	7
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W. Hyk (30%): development of the theoretical model; analysis of the experimental data; participation in the interpretation of the obtained results; participation in the manuscript preparation.

8	M. Karbarz, <b>W. Hyk</b> , Z. Stojek, “Swelling Ratio Driven Changes of Probe Concentration in pH- and Ionic Strength-Sensitive Poly(Acrylic Acid) Hydrogels” <i>Electrochemistry Communications</i> , 11 (2009) 1217–1220.	4.859	7
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W. Hyk (50%): concept of the gel synthesis; participation in the preparation of gel samples; participation in voltammetric measurements; analysis of the experimental data; participation in the interpretation of the obtained results; participation in the manuscript preparation (text, tables, figures).

9	<b>W. Hyk*</b> , Z. Stojek, “Quantifying Uncertainty of Determination by Standard Additions and Serial Dilutions Methods Taking into Account Standard Uncertainties in Both Axes” <i>Anal. Chem.</i> , 85 (2013), 5933–5939.	5.856	-
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W. Hyk (90%): theory of the regression-based method designed for the calculation of the standard uncertainty of the predictor variable either extrapolated or interpolated from a calibration line that takes into account uncertainties in both axes; theoretical basis and the procedure for the practical realization of the method of serial dilutions; Monte Carlo modeling; calculations; evaluation of the practical examples; interpretation of the obtained results; concept of the manuscript layout and its preparation (text, tables, figures); corresponding author.

10	<b>W. Hyk*</b> , D. Świącicka and S. Garboś “Application of Mixed (Bimodal) Distribution to Human Health Risk Assessment of Cu and Ni in Drinking Water Collected by RDT Sampling Method from a Large Water Supply Zone” <i>Microchemical Journal</i> , (2013) dx.doi.org/10.1016/j.microc.2013.06.002	3.048	-
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W. Hyk (40%): theory of the statistical method for the detection, quantitative characteristics, and decoupling of the mixed normal distributions (bimodal distributions); statistical calculations; evaluation of the experimental data; participation in the interpretation of the obtained results; participation in the manuscript preparation (text, tables, figures); corresponding author.

IF and number of citations are based on the Web of Science and Journal Citation Reports databases (June 03, 2013).

The research work after the Ph. D. degree covers three scientific areas. One of them is related to the theoretical modeling of the mixed diffusional and migrational transport in various

(micro- and nano-) electrochemical systems, and is presented in the series of publications (in section 4) setting the basis for the habilitation. Another area of my research work is related to the electrochemical studies of the mass transport and volume phase transitions of polymeric gels due to the variation of the environmental conditions, such as temperature, pH, and ionic strength. It is documented in the series of publications [1, 4, 5, 6, 7, 8]. I have undertaken this subject, as the first at Faculty of Chemistry, University of Warsaw, and it is now successfully realized in Laboratory of Theory of Applications of Electrodes at Faculty of Chemistry UW. Polymeric gels are defined as three-dimensional networks of connected polymeric segments swollen by a solvent. Since in some cases a gel can contain up to 99% solvent, this is a rather unusual way in which large amounts of liquid can be maintained “solid”. Therefore, gels possess many advantages characteristic of both the liquid and solid state of matter. The unique feature of polymeric gels is their existence in two states, the swollen and collapsed state. The transformation of a gel from one state to the other is generally defined as the volume phase transition. When phase transition of the gel occurs, large amount of the solution is released and the volume change of the gel system can be as large as 1000 times. The volume phase transition of the gel can be induced by chemical or physical factors, such as temperature, solvent composition, pH, ionic strength, and electromagnetic radiation. In my research work much attention has been paid to the volume phase transition and transport properties of these gels because of their potential applications in drug delivery systems, separation techniques, and construction of sensors. It resulted in the derivation of the theoretical model of mass transport in gel matrices. The model allowed one to predict diffusion coefficients of probe molecules entrapped in the gel matrix, their concentration profiles, and structural changes of the polymeric chains affected by the volume phase transition or swelling degree induced by either temperature or pH variation. The knowledge of species diffusion coefficient as a fundamental measure of molecular mobility in gels and electrostatic interactions in polyionic gels is of great importance in such applications as gel electrolytes for batteries, gel-based sensors, gels in separation techniques and polymeric gels as “solid-state” storage for liquids and their controlled release. The theoretical predictions and the concepts of experimental realization of measurements have been verified with poly(N-isopropylacrylamide) and poly(acrylate) gels. The development of the synthetic procedure for the preparation of cross-linked poly(acrylic acid) gels is another important achievement in this area. Cross-linked poly(acrylic acid) gels become model gels for studying mass transport affected by the variation of the swelling degree induced by pH changes. The strong influence of the swelling ratio of the gel on the magnitude of both diffusion coefficient and concentration of the probe molecules (sorption effects) has been demonstrated.

The series of publications [9, 10] initiates a new research area I am involved. These papers deal with the statistical and metrological aspects of chemical analysis. This subject has not been explored at Faculty of Chemistry, University of Warsaw yet. The papers present new statistical methods (tools) for data treatment in chemical analysis. The first one allows calculation of the standard uncertainty of the predictor variable either extrapolated or interpolated from a calibration line that takes into account uncertainties in both axes [9]. The mathematical scheme derived is an essential addition to the process of the analyte quantification realized with either the method of multiple standard additions or the method of serial dilutions. The latter one has been proposed as an alternative approach to the multiple standard additions procedure. The statistics of an analyte quantification via calibration line taking into account uncertainties of both variables has been already incorporated in the *e-stat* service: on-line statistical analysis in analytical laboratory (described in detail in section 5 E). The other method provides handy numerical tools for the statistical analysis of two normal or log-normal Gaussian distributions of the data taken from the heterogeneous data population [10]. The method is capable to “unmix” (decouple) bimodal distributions (mixtures of two normal or log-normal Gaussian distributions) and provides statistical characteristics for two individual modes of the mixed distribution. Both methods have been verified experimentally.

Further exploration of this research field is in progress.

## 5. C Books, monographs, book chapters, and scientific publications in journals other than included in database referred to in section 5. B

### I. Books, monographs, book chapters

	Authors, title	Editor, city, year
1	<b>W. Hyk</b> , Z. Stojek “Statistical Analysis in Analytical Laboratory” (in Polish)	1 ed., The Committee on Analytical Chemistry of the Polish Academy of Sciences, Warsaw 2000 2 ed. revised, Faculty of Chemistry, University of Warsaw, Warsaw 2006 3 ed. extended, Faculty of Chemistry, University of Warsaw, Warsaw 2010
2	<b>W. Hyk</b> , Z. Stojek, “Microelectrodes for Electroanalytical Chemistry”	Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.), John Wiley & Sons Ltd., Chichester, S1-S3 (2010) 1115-1134.

### II. List of reviewed conference materials

	Authors, title	Editor or journal, volume, year, pages
1	<b>W. Hyk</b> , Z. Stojek „Simulation of Transient Currents for Undiluted Liquid Substances at Microelectrodes”	Proceedings of the symposium on chemical and biological sensors and analytical electrochemical methods, ed. A.J. Ricco, <i>The Electrochemical Society</i> , vol. 97-19 (1997), p. 444-50.
2	<b>W. Hyk</b> , Z. Stojek „e-stat – Statistics Via the Internet” (in Polish)	<i>Analityka</i> , 4 (2001) 49.
3	<b>W. Hyk</b> , M. Ciszowska “Electrochemical Determination of Solution Storage and Release Efficiency in Thermoresponsive NIPA Gels”	Abstracts of papers of <i>the American Chemical Society</i> , 226: 354-PMSE Part 2, 2003.

## 5. D Inventions, patents, and crafts/industrial patterns

**W. Hyk**, K. Kitka

„Separation and Recovery of Silver from Materials Containing Silver, Lead and Copper”

Patent application P.400245 (positive indices in patent portfolio review)

A method of recovering silver substantially free from lead and copper from residual materials is described. The invention can be applied for metallic silver recovery from waste technological materials containing lead and copper. These may include: anodic slime from electrorefining of copper, used plating baths etc.

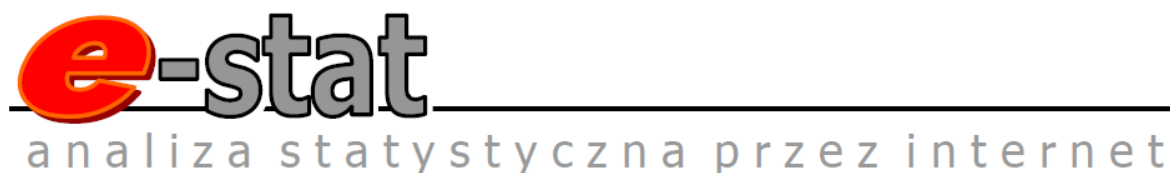


The work is realized under the research project “Greenmet Electrochem Project” listed in section 5. G

## 5. E Computer programs and systems

W. Hyk

The internet service *e-stat* “On-line Statistical Analysis in Analytical Laboratory” (in Polish and English, [www.e-stat.pl](http://www.e-stat.pl))



Nowadays web applications make www pages flexible and interactive. They are accessed by users over a network such as the internet and provide various social and scientific resources and services with no necessity for installation of specialized software on the personal computer. This convenient feature coupled to the idea of cloud computing made fundamentals for the *e-stat* service which is being developed and maintained at Faculty of Chemistry, University of Warsaw, available at [www.e-stat.pl](http://www.e-stat.pl) (using login: *e-stat* and password: AnStat).

The *e-stat* service is a collection of web-based applications for statistical calculations via the internet. They are installed on the web server of Faculty of Chemistry UW. The process of communication with a user proceeds through web pages displayed by an internet browser on user's personal computer. The applications are divided into several modules dedicated to the following groups of statistical methods (tools): basic statistical characteristics and statistical tests, linear regression methods, random error analysis, systematic error analysis, estimation of measurement uncertainty, control charts, and tables of critical values of statistical distributions. These statistical tools are extensively employed in the process of quality assurance in chemical measurements, including validation of analytical procedure; traceability of the results of chemical measurements, construction of uncertainty budget, quality control of measurements by means of control charts.

Additionally, the *e-stat* users have an opportunity to perform their analyses using novel statistical tools inaccessible in commercially available stat software. These include: construction of- and prediction from a calibration curve (or standard additions calibration line) using weighted linear regression method taking into account errors on both axes, estimation of the standard uncertainty of a chemical or physical quantity expressed implicitly. The user through its local computer sends data collected in the web form and, consequently, a request for calculations according to the method selected. The request is processed by the appropriate application using resources of the web server, and finally the calculation results along with graphical presentation are sent back to the local computer where they are displayed in a form of web page.

The *e-stat* service inspired me to reformulate some of my teaching courses. It has been successfully employed in the teaching process realized in courses of undergraduate and graduate studies at Faculty of Chemistry (University of Warsaw), Faculty of Chemistry (Warsaw University of Technology), Faculty of Management (University of Warsaw) and in postgraduate studies in Chemical Metrology. In addition to this the *e-stat* applications are now routinely used by professional analysts and quality control managers in many research and analytical laboratories of various institutions scattered all over the country. These applications

allow them either to fulfill the accreditation requirements or simply to improve implementation of good laboratory practice in their laboratories.

The growing group of the *e*-stat users makes the *e*-stat project open for new functionalities. The progress in the *e*-stat project is therefore strongly influenced by their active users. Currently, the total number of active users exceeds 180 (including 80% of institutional users).

Below, a list of institutions where the *e*-stat service is employed as of May 2013 (the academic users are not included).

#### GOVERNMENT AGENCIES

- Urząd Ochrony Konkurencji i Konsumentów, Pl. Powstańców Warszawy 1, 00-950 Warszawa
  - UOKiK, Laboratorium Kontrolno-Analityczne z siedzibą w Warszawie
  - UOKiK, Laboratorium Kontrolno-Analityczne z siedzibą w Katowicach
  - UOKiK, Laboratorium Kontrolno-Analityczne z siedzibą we Wrocławiu
  - UOKiK, Laboratorium Kontrolno-Analityczne z siedzibą w Kielcach
  - UOKiK, Laboratorium Kontrolno-Analityczne z siedzibą w Łodzi
  - UOKiK, Laboratorium Kontrolno-Analityczne z siedzibą w Bydgoszczy
- Biuro Urządzania Lasu i Geodezji Leśnej; Oddział w Krakowie, ul. Senatorska 15, 30-106 Kraków
- Mennica-Metale Szlachetne S.A., Laboratorium Analityczne, ul. Pereca 21, 00-958 Warszawa
- Izba Celna w Przemysłu, ul. Sielecka 9, 37-700 Przemysł

#### SANITARY INSPECTIONS

- Powiatowa Stacja Sanitarno-Epidemiologiczna w Legnicy, ul. Mickiewicza 24, 59-220 Legnica
- Wojewódzka Stacja Sanitarno-Epidemiologiczna w Warszawie, ul. Żelazna 79, 00-875 Warszawa
- Powiatowa Stacja Sanitarno-Epidemiologiczna w Wadowicach, ul. Teatralna 2, 34-100 Wadowice
- Wojewódzka Stacja Sanitarno-Epidemiologiczna w Poznaniu, ul. Noskowskiego 23, 61-705 Poznań
- Powiatowa Stacja Sanitarno-Epidemiologiczna w Białej Podlaskiej, ul. Warszawska 18, 21-500 Biała Podlaska
- Powiatowa Stacja Sanitarno-Epidemiologiczna w Skierniewicach, ul. Piłsudskiego 33, 96-100 Skierniewice
- Powiatowa Stacja Sanitarno-Epidemiologiczna w Suwałkach, ul. Utrata 9A, 16-400 Suwałki
- Powiatowa Stacja Sanitarno-Epidemiologiczna w Gryficach, ul. Nowy Świat 6, 72-300 Gryfice,

- Powiatowa Stacja Sanitarno-Epidemiologiczna w Nakle nad Notecią, ul. Mickiewicza 11, 89-100 Nakło nad Notecią
- Powiatowa Stacja Sanitarno-Epidemiologiczna w Iławie, ul. Sienkiewicza 10, 14-200 Iława
- Wojewódzka Stacja Sanitarno - Epidemiologiczna w Łodzi, ul. Wodna 40, 90-046 Łódź
- Powiatowa Stacja Sanitarno-Epidemiologiczna w Zduńskiej Woli, ul. Łaska 13, 98-220 Zduńska Wola
- Powiatowa Stacja Sanitarno Epidemiologiczna w Piotrkowie Trybunalski, al. 3-go Maja 8, 97-300 Piotrków Trybunalski
- Powiatowa Stacja Sanitarno Epidemiologiczna w Sochaczewie, ul. Traugutta 18, 96-500 Sochaczew

#### WATER AND SEWERAGE COMPANY / MUNICIPAL SERVICES

- Miejskie Przedsiębiorstwo Wodociągów i Kanalizacji Spółka z o. o., ul. Naruszewicza 18, 35-055 Rzeszów
- Miejskie Przedsiębiorstwo Wodociągów i Kanalizacji Sp. z o.o., ul. Lipowa 76, 64-100 Leszno
- Spółka Wodna "KAPUŚCISKA", Oczyszczalnia Ścieków, ul. Toruńska 324a, 85-880 Bydgoszcz
- Przedsiębiorstwo Usług Wodnych i Sanitarnych Sp. z o.o., ul. 700-Lecia 14/2, 72-200 Nowogard
- Wodociągi Miejskie Sp. z o.o., ul. Olsztyńska 10, 14-500 Braniewo
- Zakład Wodociągów i Kanalizacji Sp. z o. o., ul. Cegielniana 4, 05-825 Grodzisk Mazowiecki
- Zakład Wodociągów i Kanalizacji sp. z o. o., ul. Niepodległości 56, 57-400 Nowa Ruda
- Zakład Wodociągów i Kanalizacji w Gostyniu Sp. z o.o., ul. Nad Kanią 77, 63-800 Gostyń
- Wodociągi i Kanalizacja "AKWA" Spółka z o. o., Aleja Wojska Polskiego 2, 48-300 Nysa
- "Wodociągi i Kanalizacja - Zgierz" Sp. z o. o., ul. Andrzeja Struga 45, 95-100 Zgierz
- Miejskie Przedsiębiorstwo Wodociągów i Kanalizacji Spółka z o.o. w Sokółce, ul. Targowa 15, 16-100 Sokółka
- Zakład Wodociągów i Kanalizacji - Sochaczew Sp. z o. o., ul. Rozłazłowska 7, 96-500 Sochaczew
- "Wodociągi Płockie" Sp. z o.o., ul. Harcerza Antolka Gradowskiego 11, 09-402 Płock
- Zakład Wodociągów i Kanalizacji w Ciechanowie Sp. z o.o., ul. Gostkowska 81, 06-400 Ciechanów
- Przedsiębiorstwo Gospodarki Komunalnej i Mieszkaniowej w Likwidacji, ul. Piłsudskiego 111a, 36-100 Kolbuszowa

- Zakład Utylizacji Odpadów Sp. z o.o., ul. Teatralna 49, 66-400 Gorzów Wielkopolski

#### INSPECTORATES OF ENVIRONMENTAL PROTECTION

- Wojewódzki Inspektorat Ochrony Środowiska w Warszawie, ul. Bartycka 110A, 00-716 Warszawa
- Wojewódzki Inspektorat Ochrony Środowiska w Krakowie; Delegatura w Nowym Sączu, ul. Fabryczna 11, 33-300 Nowy Sącz
- Wojewódzki Inspektorat Ochrony Środowiska w Łodzi, ul. Lipowa 16, 90-743 Łódź
- Wojewódzki Inspektorat Ochrony Środowiska w Poznaniu, ul. Czarna Rola 4, 61-625 Poznań

#### VETERINARY INSPECTORATES

- Wojewódzki Inspektorat Weterynarii w Kielcach, ul. Ściegiennego 205, 25-116 Kielce
- Inspekcja Weterynaryjna, Wojewódzki Inspektorat Weterynarii we Wrocławiu, ul. Januszowicka 48, 50-983 Wrocław
- Inspekcja Weterynaryjna; Wojewódzki Inspektorat Weterynarii w Szczecinie, ul. Ostrawicka 2, 71-337 Szczecin

#### CHEMICAL AND AGRICULTURAL INSPECTIONS

- Krajowa Stacja Chemiczno-Rolnicza w Warszawie, Okręgowa Stacja Chemiczno-Rolnicza, ul. Żółkiewskiego 17 05-075 Warszawa
- Okręgowa Stacja Chemiczno-Rolnicza w Opolu, ul. Oleska 123, 45-233 Opole
- Okręgowa Stacja Chemiczno-Rolnicza w Bydgoszczy, ul. Powstańców Wielkopolskich 6, 85-090 Bydgoszcz

#### POWER STATIONS AND THERMAL POWER STATIONS

- EDF Rybnik S.A., ul. Podmiejska 44-207 Rybnik
- TAURON Ciepło S.A., ul. Grażyńskiego 49, 40-126 Katowice
- ENEA Wytwarzanie S.A., Świerże Górne; gm. Kozienice, 26-900 Kozienice 1
- TAURON Wytwarzanie Spółka Akcyjna, ul. Lwowska 23, 40-389 Katowice
- PGE Górnictwo i Energetyka Konwencjonalna S. A., ul. 1 Maja 63, 97-400 Bełchatów
- PGE GiEK S. A., ul. 1 Maja 63, 97-400 Bełchatów, PGE GiEK S. A. Oddział Elektrownia ul. Młodych Energetyków 12, 59-916 Bogatynia
- Zespół Elektrociepłowni Wrocławskich KOGENERACJA S.A., ul. Łowiecka 24, 50-220 Wrocław

#### MINING AND METALLURGICAL COMPANIES

- Zakład Odmetanowania Kopalń ZOK Sp. z o.o. ul. Boczny 24, 44-335 Jastrzębie-Zdrój
- Centrum Badań i Dozoru Górnictwa Podziemnego Sp. z o. o. ul. Lędzińska 8, 43-143 Łędziny
- KGHM, Centrum Badań Jakości spółka z ograniczoną odpowiedzialnością, ul. M. Skłodowskiej-Curie 62, 59-301 Lubin
- CELSA "Huta Ostrowiec" Sp. z o. o., ul. Samsonowicza 2, 27-400 Ostrowiec Świętokrzyski
- Lubelski Węgiel "Bogdanka" S.A., Bogdanka, 21-013 Puchaczów
- Południowy Koncern Węglowy S.A., ul. Grunwaldzka 37, 43-600 Jaworzno
- Przedsiębiorstwo Górnicze "SILESIA" Sp. z o.o., ul. Górnicza 60, 43-502 Czechowice-Dziedzice

#### FUEL DISTRIBUTION AND INDUSTRY

- Polskie Górnictwo Naftowe i Gazownictwo S. A. w Warszawie, Oddział w Zielonej Górze, ul. Boh. Westerplatte 15, 65-034 Zielona Góra
- Operator Logistyczny Paliw Płynnych Sp. z o.o., ul. Wyszogrodzka 133, 09-410 Płock
- LOTOS Lab Sp. z o.o., ul. Elbląska 135, 80-718 Gdańsk

#### CHEMICAL COMPANIES

- Laboratorium Badawcze Blachownia Sp. z o.o., ul. Szkolna 15, 47-225 Kędzierzyn-Koźle
- ZAK Spółka Akcyjna, ul. Mostowa 30A, 47-220 Kędzierzyn-Koźle
- Zakłady Chemiczne "Organika-Sarzyna" S.A., ul. Chemików 1, 37-310 Nowa Sarzyna
- ICSO CHEMICAL PRODUCTION Spółka z o.o., ul. Energetyków 4, 47-225 Kędzierzyn - Koźle

#### NATIONAL RESEARCH INSTITUTES

- Instytut Ochrony Roślin - Państwowy Instytut Badawczy, ul. Węgorka 20, 60-318 Poznań
- Instytut Technologiczno-Przyrodniczy, al. Hrabska 3 Falenty, 05-090 Raszyn
- Instytut Ceramiki i Materiałów Budowlanych, Oddział Szkła i Materiałów Budowlanych, ul. Cementowa 8, 31-983 Kraków
- Instytut Biotechnologii Surowic i Szczepionek, BIOMED SA, Al. Sosnowa 8, 30-224 Kraków
- Instytut Uprawy Nawożenia Gleboznawstwa – PIB, ul. Czartoryskich 8, 24-100 Puławy
- Instytut Ochrony Roślin - Państwowy Instytut Badawczy, ul. Węgorka 20, 60-318 Poznań

- Instytut Podstaw Inżynierii Środowiska PAN, ul. M. Skłodowskiej-Curie 34, 41-819 Zabrze
- IMGW - PIB, ul. Podleśna 61, 01-673 Warszawa
- Instytut Zootechniki, Państwowy Instytut Badawczy; Krajowe Laboratorium Pasz, ul. Chmielna 2, 20-079 Lublin
- Instytut Żywności i Żywienia, ul. Powsińska 61/63, 02-903 Warszawa
- Instytut Biotechnologii Przemysłu Rolno-Spożywczego, Oddział Technologii Mięsa i Tłuszczu, ul. Jubilerska 4, 04-190 Warszawa
- Instytut Zootechniki; Państwowy Instytut Badawczy; Krajowe Laboratorium Pasz, ul. Żubrów 1, 71-617 Szczecin
- Instytut Ochrony Środowiska, ul. Krucza 5/11, 00-548 Warszawa
- Centralny Ośrodek Badawczo-Rozwojowy Opakowań, ul. Konstancińska 11, 02-942 Warszawa

#### GEOLOGICAL COMPANIES

- Przedsiębiorstwo Geologiczne Sp. z o.o., ul. Hauke Bosaka 3A, 25-214 Kielce
- Przedsiębiorstwo Geologiczne "POLGEOL" S.A., ul. Berezynska 39, 03-908 Warszawa
- PETROGEO Przedsiębiorstwo Usług Laboratoryjnych i Geologicznych Sp. z o.o., ul. Łukasiewicza 11, 05-200 Wołomin

#### DAIRY COOPERATIVES

- Podkarpackie Laboratorium Oceny Mleka Sp. z o.o., Trzebowniko 931, 36-001 Trzebowniko
- Okręgowa Spółdzielnia Mleczarska Garwolin, ul. Ogrodowa 17, 08-410 Wola Rębkowska

#### OTHER MEASUREMENT LABORATORIES

- LAB-CENTRUM Przedsiębiorstwo Handlowe, Fabian Kowalów, ul. Szygarska 39, 41-608 Świętochłowice
- Firma Projektowo - Usługowo - Badawcza, Ekowizjer, Zbigniew Walaszczyk, ul. Topolowa 2, 41-600 Świętochłowice
- JARS Sp. z o.o., Łajski, ul. Kościelna 2 a, 05-119 Legionowo
- Ekoanalitka Jerzy Sternal, ul. Święciechowska 4, 64-100 Leszno
- Przedsiębiorstwo Wielobranżowe Labora s. c., ul. Bazylianówka 39, 20-144 Lublin
- Niezależne Laboratorium Badawcze "Stanlab" Sp. z o.o. ul. Bydgoska 1a, 89-100 Nakło nad Notecią
- Zakład Badań Środowiska "VIBROSON" S.C.; mgr E. Mazik, T. Wnuk, ul. Piłsudskiego 83, 42-500 Będzin

- Specjalistyczne Laboratorium Badawcze "ITA TEST" S.C., ul. Obozowa 82A paw.1, 01-434 Warszawa
- PAK Centrum Badań Jakości Sp. z o. o., ul. Przemysłowa 158, 62-510 Konin
- BOL-THERM Sp. z o. o., . Kolejowa 37, 32-332 Bukowno
- Przedsiębiorstwo Wielobranżowe Prima Sp. z o.o. ul. Gośniewska 46, 05-660 Warka
- Silliker Polska Sp. z o.o., ul. Żeromskiego 17, 01-882 Warszawa
- Przedsiębiorstwo Produkcyjno-Handlowo-Usługowe "Pro-Lab" Sp. z o. o., ul. Toruńska 222, 87-800 Włocławek
- Centralne Laboratorium Pomiarowo-Badawcze Sp. z o. o. ul. Rybnicka 6, 44-335 Jastrzębie Zdrój
- Pracownia Badań Środowiska Pracy "Higiena Pracy" Marek Smoczyński, ul. Jasna 3b/7, 59-400 Jawor
- "LabAnalityka" Sp. z o.o., ul. Sienkiewicza 4, 56-120 Brzeg Dolny
- Grupa Interlis S.C., Piotr Kaczmarek, Hanna Kaczmarek, ul. Wolica 93c, 62-872 Godziesze
- Wessling Polska sp. z o. o., ul. Bobrzyńskiego 14, 30-348 Kraków
- Laboratorium Analiz Lekarskich mgr P. Zieliński, ul. M. C. Skłodowskiej 11, 44-200 Rybnik
- 26 Wojskowy Oddział Gospodarczy, JW 4809, WOMP Modlin, ul. Juzistek 2, 05-131 Zegrze
- "Polcargo-Medyka" Sp. z o. o. 37-732 Medyka 161
- Jednostka Ratownictwa Chemicznego Sp. z o. o., ul. Kwiatkowskiego 8, 33-101 Tarnów

## 5. F Presentations at international and national conferences (without poster presentations)

### I. Invited lectures

	Title	Conference name, venue, year
1	“Electrochemical Studies On Transport Properties of Polymeric Gels”	49 Meeting of the Polish Chemical Society, Gdańsk 2006
2	„e-stat – Statistical Analysis Via the Internet” (in Polish)	XIV POLLAB Symposium, Jurata 2008
3	„Uncertainty Budget – a Key Element in the Process of Quality Assurance in Research Work” (in Polish)	X Conference on „Chemical Analysis for Hydrogeology and Environmental Protection”, Polish Geological Institute, Warsaw 2009
4	„On Effective Cooperation of Universities with Business Partners” (in Polish)	MACULEWICZ CONSULTING, Warsaw 2013
5	„Quality Control in Laboratories” (in Polish)	„Novel Systems and Instrumentation in Laboratory of XXI Century” the Polish Chemical Society, Warsaw 2013

## II. Lectures

	Title	Conference name, venue, year
1	„The Extreme Migrational Enhancement of Faradaic Current at Microelectrodes. Experimental and Theoretical Studies”	55th Annual Meeting of the International Society of Electrochemistry, Thessaloniki, Greece, 2004
2	„Electrochemical Studies on Efficiency of Solute Release from Thermoresponsive Gels”	Polymer gels and networks : 44th Microsymposium of P.M.M., Prague, Czech Republic, 2005
3	“Steady-State Operation of Porous Photoelectrochemical Cells Under the Conditions of Mixed Diffusional and Migrational Mass Transport. Theory”	211th Meeting of the Electrochemical Society, Chicago, USA, 2007
4	„Simultaneous Determination of Probe Concentration and Diffusion Coefficient in Polymeric Hydrogels”	214th Meeting of the Electrochemical Society and 2008 Fall Meeting of The Electrochemical Society of Japan, Honolulu, USA, 2008
5	„Analyte Quantification Using Linear Calibration Function Taking into Account Standard Uncertainties of Both Variables” (in Polish)	V Conference on „Chemometrics – Methods and Applications”, Zakopane 2012

### 5. G Leadership in research projects and participation in such projects

1) **3 T09A 003 12** (research grant for young scientist, the Polish State Committee for Scientific Research, 1997)

“Various Aspects of Modeling of Diffusion and Migration”

**Grant Manager**

2) **3 T09A 076 17** (grant for Ph. D. student, the Polish State Committee for Scientific Research, 1999)

**Main Contractor**

3) **3 T09A 087 27** (research grant, the Polish Ministry of Scientific Research and Information Technology, 2005 - 2007)

**Main Contractor**

4) **BW-172106, BW-179202** (research grants, Faculty of Chemistry, University of Warsaw, 2006, 2008)

„Smart Gels – New Medium for Electrochemistry”

**Grant Manager**



5) **N-N204 244534** (research grant, the Polish Ministry of Science and Higher Education, 2008 - 2010)

**Contractor**

6) **Greenmet Electrochem Project, UDA-POIG.01.04.00-14-069/11** (Innovative Economy Programme (1.4) in cooperation with Greenmet Sp. z o.o., 2012 – 2013)

„Development and Implementation of Novel Technology for Recovery of Metals of High Purity”



**Grant Manager**

**6. Additional information**

**6. A Teaching activities**

Course name		Course type ( <b>field of study</b> , department)
<i>Undergraduate studies (I level)</i>		
1	General Chemistry (in Polish)	Seminar ( <b>Chemistry</b> , Faculty of Chemistry, University of Warsaw)
2	Inorganic Chemistry (in Polish)	Laboratory ( <b>Nanostructure Engineering, and Nuclear Power Engineering and Nuclear Chemistry</b> , Faculty of Chemistry, University of Warsaw)
3	Chemical Analysis in Environmental Research (in Polish)	Laboratory ( <b>Inter-Faculty Studies in Environmental Protection</b> , Faculty of Chemistry, University of Warsaw)
<i>Graduate studies (II level)</i>		
1	Environmental Statistics and Modeling	Lecture and computer exercises ( <b>Environmental Management</b> , Faculty of Chemistry, Faculty of Biology, and Faculty of Management, University of Warsaw)
2	Data Treatment in Biotechnology	Computer exercises ( <b>Applied Biotechnology</b> , Faculty of Chemistry, Warsaw University of Technology)
3	Environmental Analysis (in Polish)	Computer exercises ( <b>Chemistry</b> , Faculty of Chemistry, University of Warsaw)
4	Validation of Analytical Methods (in Polish)	Specialization laboratory ( <b>Chemistry</b> , Faculty of Chemistry, University of Warsaw)
<i>Postgraduate studies</i>		

1	Quality Control in Measurements (in Polish)	Lecture and computer exercises ( <b>Metrology in Chemistry</b> , Faculty of Chemistry, University of Warsaw)
2	Validation and Estimation of Uncertainty of Analytical Procedures (in Polish)	Lecture and computer exercises ( <b>The Application of Chemistry in Environmental Protection</b> , Faculty of Chemistry, University of Warsaw)
3	Information Technology in Chemistry (in Polish)	Computer exercises ( <b>Post Graduate Studies for Teachers in Chemistry</b> , Faculty of Chemistry, University of Warsaw)

#### 6. B Scientific assistance to students as scientific supervisor

- Supervisor of Bachelor degree theses: 2
- Supervisor of M. Sc. degree theses: 4
- Supervisor of Postgraduate degree theses: 203 (Postgraduate Studies in Metrology in Chemistry)

#### 6. C Reviews of publications in international and national journals

- Electroanalysis: 1 review
- Chemia Analityczna: Chemical Analysis: 2 reviews
- Journal of Physical Chemistry A: 1 review
- Sensors and Actuators B: Chemical: 1 review

#### 6. D Participation in organizing committees of international and national scientific conferences

- 2000 – a member of the Local Organizing Committee of *51st Annual Meeting of the International Society of Electrochemistry* (Warsaw, Poland). An author of the interactive web service of the conference, on-line services for the conference registration and abstract submission, conference brochures, and the interactive book of abstracts in the electronic form.

#### 6. E Internships in foreign research and academic centers

- 2002 – 2003: Postdoctoral Research Assistant, Department of Chemistry, Brooklyn College, the City University of New York (NY, USA)
- 2005 / 2006: Postdoctoral Fellow, Department of Inorganic, Analytical and Applied Chemistry, University of Geneva (Geneva, Switzerland)

#### 6. F International and national awards for scientific and teaching achievements

- 1999 – Stipend of the Foundation for Polish Science
- 2002 – Wiktor Kemula Award (Polish Society of Chemistry) for distinctive research papers

